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ÉTUDE DE LA PHÉNYL-2 OXINE ET DE SES CHÉLATES

II. CONSTANTES DE DISSOCIATION DE LA PHÉNYL-2 OXINE

par

GEORGES BOCQUET ET RENÉ A. PÂRIS

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Des valeurs des constantes d'ionisation

$$K_1 = \frac{[HPhOx]\ [H^+]}{[H_2PhOx^+]} \quad \text{et} \quad K_2 = \frac{[PhOx^-]\ [H^+]}{[HPhOx]}$$

de la phényl-2 oxine (HPhOx) ont été obtenues par potentiométrie et par spectrophotométrie. Etant donnée la faible solubilité du réactif dans l'eau[1], les mesures ont été faites sur des solutions hydroalcooliques. La présence d'alcool dans le milieu a une influence marquée sur la dissociation: les valeurs obtenues n'ont donc de signification que pour le milieu considéré.

MÉTHODES

1. La méthode potentiométrique consiste à suivre la variation du pH en fonction du volume de base (ou d'acide) ajouté à une solution acide (ou basique) du composé étudié. La neutralisation d'une forme ionique se traduit sur la courbe par la présence d'un "palier" compris entre deux "sauts" de pH; en première approximation le pK est égal au pH au point de demi-neutralisation.
2. La méthode spectrophotométrique d'après STENSTRÖM ET GOLDSMITH[2] consiste à construire la courbe représentant en fonction du pH, le coefficient d'extinction à une longueur d'onde convenablement choisie, et à déterminer graphiquement le point où l'extinction est la moyenne de ses valeurs en milieu neutre et en milieu fortement acide (ou basique). En un tel point le pH est égal, en première approximation, au pK cherché.

INFLUENCE DE L'ALCOOL SUR LA DISSOCIATION DE L'OXINE

Pour mettre en évidence l'effet de la présence d'une certaine teneur d'alcool dans le milieu sur les constantes d'ionisation, nous avons tracé, avec l'oxine, les courbes potentiométriques de la Fig. 1: l'une en milieu aqueux, l'autre en milieu hydroalcoolique

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à 45° G.L., les autres conditions étant identiques (10^{-3} mole d'oxine; volume initial 80 ml; HCl $N/40$). Les points d'inflexion A, I et B correspondent aux sauts de pH; P_1 et P_2 sont les points de demi-neutralisation.

Ces courbes fournissent les valeurs suivantes des constantes de l'oxine:

milieu aqueux :

$pK_1 = 5.10$ $pK_2 = 9.90$

milieu hydroalcoolique:

$pK_1 = 4.55$ $pK_2 = 10.75$

On voit que l'addition d'alcool fait subir à l'oxine un très net recul d'ionisation, aussi bien du côté acide que du côté basique.

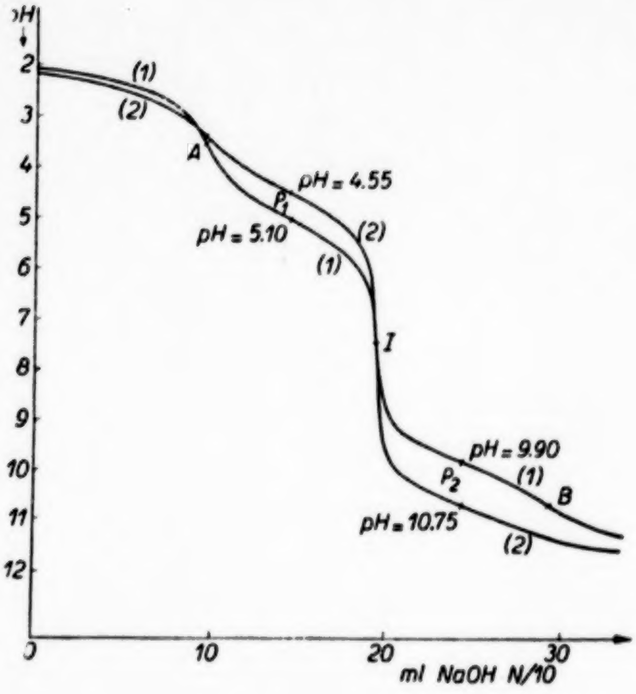

Fig. 1. Courbes de neutralisation de l'oxine. Temp. = 20° C.
Courbe (1) : milieu aqueux.
Courbe (2) : milieu hydroalcoolique 45° G.L.

CONSTANTES DE DISSOCIATION DE LA PHÉNYL-2 OXINE

A - Méthode potentiométrique (milieu hydroalcoolique 45° G.L.)

La courbe 3 de la Fig. 2 a été obtenue dans des conditions analogues à la courbe 2 de la Fig. 1: seule diffère la concentration du réactif ($5 \cdot 10^{-4}$ mole de phényl-2 oxine au lieu de 10^{-3} mole

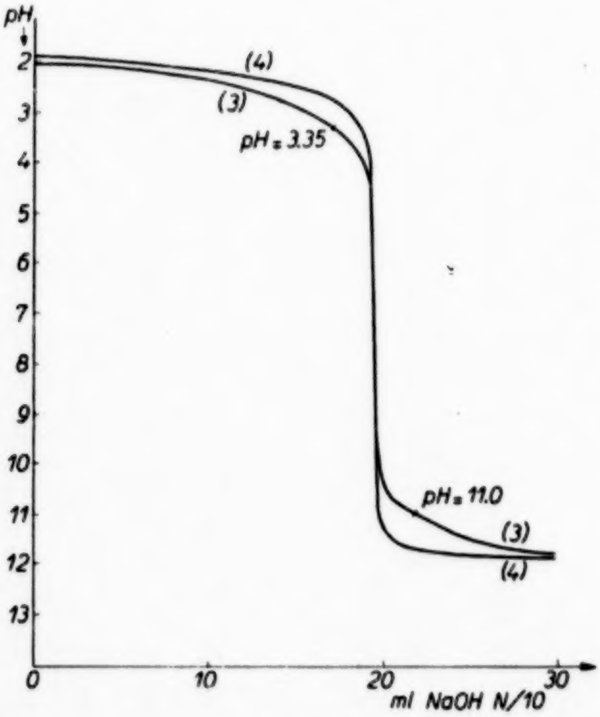

Fig. 2. Courbes de neutralisation en milieu hydroalcoolique à 45° G.L. Temp. = 17° C.
Courbe (3) : Avec phényloxine.
Courbe (4) : Sans „

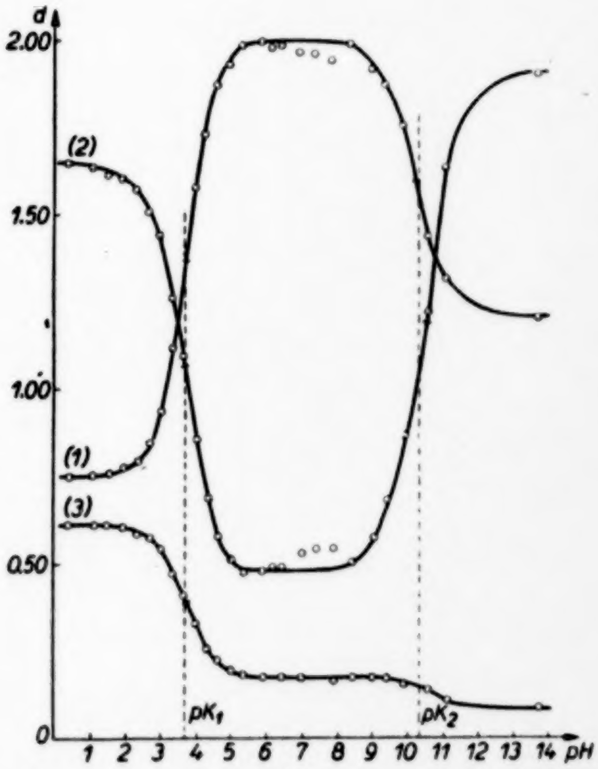

Fig. 3. Phényloxine C = 10 mg/l. Milieu hydroalcoolique 20° G.L. (1) : d_{270}, (2) : d_{285}, (3): d_{340} en fonction du pH. Cuves de 1.00 cm.

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d'oxine), donc la position des sauts de pH. Ces sauts de pH sont très peu marqués; ils apparaissent cependant par comparaison avec la courbe de neutralisation acide-base dans le même milieu (courbe 4).

De ces courbes de neutralisation de la phényl-2 oxine on peut en déduire les valeurs suivantes des constantes:

$$pK_1 = 3.35 \qquad pK_2 = 11.0$$

B - Méthode spectrophotométrique (milieu hydroalcoolique 20° G. L.)

Pour appliquer cette méthode, nous avons déterminé les densités optiques à 270, 285 et 340 mµ de solutions tamponnées à 10 mg/l de phényl-2 oxine en milieu hydroalcoolique à 20° G.L.: le choix de ces conditions découle des résultats précédemment exposés[1] concernant la solubilité de la phényl-2 oxine et l'évolution de son spectre ultraviolet, en fonction du pH.
La concentration en phényl-2 oxine étant uniforme, les courbes (Fig. 3) ont été construites en portant directement la densité optique en fonction du pH.

Les valeurs obtenues par cette méthode et les précédentes sont rassemblées dans le Tableau I.

TABLEAU I

	Oxine		*Phényl-2 oxine*	
	milieu aqueux	*milieu hydroalcoolique à 45° G.L.*		*id. 20° G.L.*
pK_1	5.10	4.55	3.35	3.70
pK_2	9.90	10.75	11.0	10.4

Ces chiffres font apparaître d'une part l'influence de l'alcool sur les constantes de dissociation (recul d'ionisation), et d'autre part, l'effet du substituant — C_6H_5, en particulier sur la basicité de l'atome d'azote qui se trouve fortement diminuée.

RÉSUMÉ

Les auteurs ont déterminé, par potentiométrie et par spectrophotométrie, les constantes de dissociation de la phényl-2 oxine en milieu hydroalcoolique.

SUMMARY

The authors determined, by spectrophotometric and potentiometric methods, the ionization constants of 2-phenyl-8-quinolinol in hydroalcoholic solutions.

ZUSAMMENFASSUNG

Die Verfasser haben die Ionisationskonstanten des 2-Phenyloxins in hydroalkoholischer Lösung durch potentiometrische und spektrophotometrische Methoden bestimmt.

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INSOLUBLE SUBSTANCES IN QUALITATIVE ANALYSIS

by

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In earlier publications[1,2] from this laboratory a new scheme of qualitative analysis based on the decomposition of thiosalts was put forward. In this scheme the original mixture was evaporated to dryness with concentrated nitric and hydrochloric acids successively, the residue was taken up with dilute hydrochloric acid and the resulting mixture oxidized with bromine water and filtered. The filtrate containing the soluble salts was treated with alkali sulphide reagent for the detection of basic radicals and the undissolved residue was tested for insoluble substances.

No systematic scheme for the detection of insoluble substances has yet been devised. Most textbooks on qualitative analysis give merely a list of compounds which are termed "insoluble substances" and a certain number of general tests which may be applied one after another to detect these substances in the insoluble residue. There is not only no definite scheme for the identification of the so-called insoluble substances but there is also no agreement among different authors with regard to the inclusion of different compounds in the list of insoluble substances. Many compounds are classed as insoluble substances by some authors and not by others. This must naturally be confusing to the ordinary student, who has not only no definite scheme to guide him in the analysis of the insoluble residue, but does not even know which compounds to look for in such a residue.

When one considers how thoroughly the methods for the identification of acids and bases in qualitative analysis have been systematized there does not appear to be any reason why a similar scheme should not also be available for the systematic detection of insoluble substances. With such a scheme the student would no doubt be able to tackle this problem with more confidence and less chance of error.

Before such a scheme can be devised it is necessary to have a clear understanding of the behaviour of substances which may be considered to be insoluble. There is considerable uncertainty in the mind of the ordinary student chiefly because of the discrepancies on this point in the current textbooks of qualitative analysis. Many substances such as fused lead chromate and mercuric sulphide, which are sometimes classed as insoluble substances dissolve easily, provided the mixture is evaporated to dryness successively with concentrated nitric and hydrochloric acids, and there is no reason why they should be classed as insoluble substances. On the other hand there are many substances such as the ignited phosphates of titanium, thorium,

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cerium and tin, and the ignited oxides of thorium, cerium and zirconium, which are not generally included in the list of insoluble substances, but which behave in such a manner as to justify their inclusion.

Because of these discrepancies and uncertainties a systematic study of all substances of this class has been undertaken. A knowledge of the behaviour of such substances towards acids which are used in separating the soluble from the insoluble portion of the mixture is especially important, because it will enable us to decide which compounds should be classed with the insoluble substances and also make it possible to achieve a satisfactory separation of the soluble and insoluble portions of the mixture.

In the recommended procedure for the separation, the original mixture is evaporated to dryness with concentrated nitric and hydrochloric acids successively to ensure the solution of the compounds which require an oxidizing or reducing acid solvent. However, a study of this problem has shown that the detection of insoluble compounds is rendered appreciably simpler if the mixture is also subjected to the action of aqua regia before the insoluble portion is separated by filtration. If, therefore, a preliminary examination of the mixture shows the presence of insoluble substances, it is better to add concentrated hydrochloric acid when about 5 ml of concentrated nitric acid is left. It has been found that this procedure enables us to utilize the oxidizing action of aqua regia without interfering with the reducing action of concentrated hydrochloric acid. Substances such as manganese dioxide and lead peroxide, which require a reducing acid solvent, dissolve easily when this modified procedure is followed and a large number of substances such as AgBr, AgI, AgCN, AgCNS, $Ag_4[Fe(CN)_6]$, $Ag_3[Fe(CN)_6]$, $Zn_2[Fe(CN)_6]$, WS_3, $PtCl_2$ and AuCl, which would otherwise be left with the insoluble residue are eliminated. The insoluble silver salts are all converted into AgCl, $Zn_2[Fe(CN)_6]$ is completely decomposed, WS_3 is converted into tungstic oxide and the chlorides of gold and platinum pass into solution.

In order to restrict the scope of the work, insoluble compounds of only those elements which are included in the new scheme of qualitative analysis have been studied and included in the present scheme. Minerals have also been excluded. Before discussing the scheme for the detection of insoluble substances it is necessary to review briefly their relevant properties. These compounds are discussed below.

Sulphates: One has to consider the sulphates of barium, strontium, chromium (anhydrous) and lead as being insoluble. The first three do not dissolve to any appreciable extent in concentrated hydrochloric or nitric acids or aqua regia. The behaviour of lead sulphate is dependent upon the conditions of the experiment. One gram of lead sulphate when present alone dissolves completely after being evaporated to dryness with 20 ml of concentrated hydrochloric acid. However, if soluble sulphate is also present together with lead sulphate, a considerable portion of the salt remains undissolved. If, for example, one gram of lead sulphate is evaporated to dryness with one gram of potassium bisulphate, about 20% of the salt is found to remain in the insoluble residue. From this it will be clear that lead sulphate should be classed with the insoluble substances despite its solubility in concentrated hydrochloric acid.

Halides: AgCl, AgBr, AgI, $CrCl_3$ (violet), AuCl and $PtCl_2$ are generally classed with the insoluble substances. Of these AgBr and AgI are converted into AgCl, and AuCl and $PtCl_2$ are dissolved, on treatment with aqua regia. Thus, if the original mixture is treated with aqua regia, only AgCl will be found in the insoluble residue. Violet chromium chloride does not dissolve to any appreciable extent in aqua regia. Ordinary samples of violet chromium chloride seem to contain some soluble chloride, since on boiling with concentrated acids about 10% of the salt dissolves. The portion that remains undissolved is not affected by further treatment with concentrated acids. The violet chromium chloride unlike the anhydrous chromium sulphate is decomposed easily by boiling with dilute caustic soda solution, chromium hydroxide being precipitated. The sulphate is decomposed only to a slight extent by boiling with concentrated caustic soda solution.

Among fluorides only that of calcium (fluorspar) is considered as insoluble, but the compound dissolves to a considerable extent in concentrated hydrochloric acid. Thus when 0.5 g of fluorspar is evaporated to dryness with 20 ml of concentrated hydrochloric acid only a residue of silica remains, all the calcium fluoride having passed into solution. However, as a portion of the calcium fluoride may remain undissolved when larger quantities are taken it is safer to make provision for its detection in the insoluble residue. Investigations have shown that another fluoride, that of thorium, must be included in the list of insoluble substances. If thorium fluoride is dried at a temperature of 100° C, or ignited, it remains undissolved on evaporation with concentrated acids or aqua regia to the extent of about 80%. It is, therefore, more insoluble than natural calcium fluoride.

Phosphates: Phosphates do not generally figure in the list of insoluble substances but investigations have shown that the phosphates of five metals — zirconium, titanium, cerium (ic), thorium and stannic tin — are very difficultly soluble especially when ignited and are likely to be found in the insoluble residue. Of these, zirconium phosphate is the most insoluble, even freshly precipitated zirconium phosphate remaining undissolved on evaporation with concentrated acids. The other four phosphates, when freshly precipitated, dissolve completely in concentrated hydrochloric acid, but are partially reprecipitated on dilution, with the exception of cerium, which remains in solution because of its prior reduction to the cerous state. If concentrated nitric acid is used instead of concentrated hydrochloric acid the phosphates of titanium and thorium behave similarly, but in the case of cerium and stannic tin the behaviour is different. Cerium phosphate is also partially precipitated from nitric acid solution on dilution. Stannic phosphate is insoluble in concentrated nitric acid.

Ignition of these four phosphates brings about considerable changes in their solubility in acids. If titanium phosphate is ignited for 2-4 hours over a Bunsen flame it is rendered completely insoluble in concentrated acids. Ignition over a blowpipe appears, however, to decompose it partially since it is then partly soluble in concentrated hydrochloric acid. If ceric phosphate is ignited for 2-4 hours over a Bunsen burner or over a blowpipe flame a small portion (about 5%) dissolves in concentrated acids, the residue being unaffected by further treatment with the acids. Stannic phosphate is rendered completely insoluble in concentrated acids by ignition for 2-4 hours. Thorium phosphate becomes much less soluble on ignition. It is only when the ignited phosphate is evaporated to dryness with concentrated hydrochloric acid four to five times that it passes completely into solution. The ignited phosphate is therefore sufficiently insoluble to leave a residue after the standard treatment for the separation of insoluble substances.

It will be seen from the above discussion that all the five phosphates will be found in the insoluble residue after the standard treatment with concentrated acids provided the phosphates have been ignited previously. They are all decomposed by fusion with sodium hydroxide and sodium carbonate, the phosphate passing into solution and the tin, titanium, thorium, cerium and zirconium being converted respectively into sodium stannate and sodium titanate, which are soluble in water and thorium oxide, ceric oxide and sodium zirconate, which are insoluble.

Oxides: The ignited oxides of aluminium, chromium, titanium, tin, antimony (Sb_2O_4) and silicon are well known as insoluble substances. There are five other oxides which are not generally included in the list of insoluble substances but which should be placed in it. These are the ignited oxides of zirconium, thorium, cerium (ic), molybdenum (MoO_3) and tungstic acid. If the oxides of zirconium and thorium are strongly ignited they are rendered so insoluble that even after treatment with concentrated hydrochloric acid most of the oxide is left in the residue. Thus when a 0.5 g sample of ignited oxide of thorium is evaporated almost to dryness with 20 ml concentrated hydrochloric acid about 93% of the oxide remains undissolved in the acid. Similar treatment of ignited zirconium oxide leaves about 99% of the oxide undissolved. Tungstic acid, even without prior ignition, remains completely undissolved in concentrated acids. The behaviour of ceric oxide is peculiar. Ordinary ceric oxide, even after strong ignition, dissolves completely in concentrated hydrochloric acid, but if it is fused with sodium hydroxide it is rendered insoluble in concentrated nitric and hydrochloric acids or aqua regia though it dissolves in concentrated sulphuric acid and is converted into soluble ceric sulphate by fusion with potassium bisulphate. If freshly precipitated molybdic acid is heated at a temperature of 120° C, it can still be dissolved in dilute hydrochloric acid, but ignition for 2-4 h renders it difficultly soluble, only 50% being dissolved by the standard acid treatment.

Since the ignited oxides are detected by fusion with sodium hydroxide and sodium carbonate, it is necessary to note their behaviour on such fusion. Aluminium, chromium, tin and antimony form salts which are soluble in water. Zirconium oxide is converted by such fusion into sodium zirconate, which is insoluble in water but is soluble in concentrated hydrochloric acid. Titanium oxide is converted into sodium titanate, which on boiling with water gives by hydrolysis titanium oxide, which, being freshly precipitated, dissolves completely in concentrated hydrochloric acid. Thorium oxide on fusion with alkali remains practically unaffected, less than 10% dissolving in concentrated hydrochloric acid after such a fusion. It dissolves completely only after fusion with an acid flux such as potassium hydrogen sulphate.

Sulphides: There are two sulphides which are difficultly soluble in concentrated hydrochloric or nitric acids, but dissolve easily in aqua regia: HgS and SnS_2 (mosaic gold). WS_3 is converted by heating with concentrated acids into $WO_3 . H_2O$. If these sulphides are present in the mixture, only tungsten will remain in the insoluble residue after the standard treatment for the separation of insoluble substances. HgS and SnS_2 are not affected by boiling with sodium carbonate solution, while WS_3 dissolves. So the sodium carbonate extract, as well as the residue should be tested for the sulphide radical.

Complex cyanides: There are three ferricyanides, those of silver, copper and ferrous iron and five ferrocyanides, those of ferric iron, silver, copper, uranium and zinc which are generally included in the list of insoluble substances. Zinc ferrocyanide is decomposed and dissolved completely on treatment with aqua regia and cannot therefore be found in the insoluble residue after the standard acid treatment. Silver ferro- and ferricyanides are converted by aqua regia into silver chloride and the ferro- and ferricyanide radicals are completely decomposed. Copper ferro- and ferricyanides are not affected either by concentrated nitric acid or hydrochloric acid, but are dissolved to a slight extent by aqua regia. Uranyl ferrocyanide is not affected by concentrated hydrochloric or nitric acid, but is dissolved with difficulty in aqua regia, two to three evaporations being necessary to dissolve it completely. It is, therefore, very likely to be present in the insoluble residue after the standard acid treatment. Turnbull's blue remains undissolved by aqua regia, while Prussian blue is dissolved to a slight extent.

All these ferro- and ferricyanides are easily decomposed by boiling with sodium hydroxide and sodium carbonate solution, the ferro- and ferricyanide radicals passing into the filtrate and the metals remaining with the insoluble residue as hydroxide or as sodium diuranate in the case of uranium.

Other compounds: Silver cyanide and thiocyanate are generally included in the list of insoluble substances. Both are converted by aqua regia into silver chloride. The acid radicals of these two salts are decomposed by aqua regia. In order to test for the acid radicals the original mixture should be treated with zinc and dilute sulphuric acid, since these two silver salts are not decomposed by boiling with sodium carbonate solution. Fused lead chromate dissolves easily even in concentrated hydrochloric acid and there is no reason why it should be classed with the insoluble substances.

From a detailed discussion of the properties of those substances which may be considered to be insoluble it is clear that the following are likely to be present in the residue after the standard treatment with concentrated nitric acid and hydrochloric acid in such a manner that the latter is added when about 5 ml of nitric acid is left and aqua regia is thus formed in the intermediate stage.

$BaSO_4$, $SrSO_4$, $Cr_2(SO_4)_3$ (anhydrous), $PbSO_4$
$AgCl$, $CrCl_3$, CaF_2, ThF_4
$Zr(HPO_4)_2$, $Ti(HPO_4)_2$, $Ce(HPO_4)_2$, $Th(HPO_4)_2$, $Sn_3(PO_4)_4$.
Prussian blue, Turnbull's blue, cupric ferro- and ferricyanides and uranyl ferrocyanide.
Al_2O_3, Cr_2O_3, SnO_2, Sb_2O_4, SiO_2, ZrO_2, TiO_2, ThO_2, CeO_2, WO_3, MoO_3.

The following steps may be taken to identify systematically the compounds present in the insoluble residue.

Procedure I. Extract the residue with saturated ammonium acetate solution to dissolve out $PbSO_4$ and test the solution for lead.

Procedure II. Boil the insoluble residue with 4*N* sodium hydroxide solution and filter.
(a) WO_3 and MoO_3 dissolve completely
(b) $CrCl_3$ forms sodium chromite, which gives a precipitate of $Cr(OH)_3$ on boiling
(c) Al_2O_3, Sb_2O_4 and SiO_2 may dissolve partially
(d) Ferro- and ferricyanides will be decomposed completely with the precipitation of metallic hydroxides in the case of iron and copper, and of $Na_2U_2O_7$ in the case of uranium. The metallic hydroxides and $Na_2U_2O_7$ remain on the filter paper along with the other undecomposed insoluble substances while the ferro- and ferricyanides pass into the filtrate.

The filtrate is concentrated to a small volume, evaporated to dryness with aqua regia to dehydrate silica and decompose the ferro- and ferricyanides. The residue is taken up with hot $2N$ hydrochloric acid, filtered and analysed as follows:

Ppt : $SiO_2.H_2O$, $WO_3.H_2O$ Divide into two parts (1) Test one part for W with Zn and HCl. (2) Test the second part for Si by SiF_4 test in a lead crucible.	Filt.: chlorides of Al, Cr, Fe, Mo and Sb. Treat with excess of $1N$ Na_2S and filter.		
	Ppt.: $Al(OH)_3$ $Cr(OH)_3$ Fe_2S_3 Test as usual.	Filt.: Thiosalts of Mo and Sb Acidify and boil with $6N$ HCl and filter.	
		Ppt.: MoS_3 Test as usual	Filt.: $SbCl_3$ Test as usual

The precipitate obtained after boiling with $4N$ sodium hydroxide solution is extracted with dilute hydrochloric acid and the solution containing the chlorides of Fe, Cr, Cu and U analysed as follows:

Add $1N$ Na_2S in excess and filter. Treat the precipitate of hydroxides and sulphides with dil. HCl and filter.

Ppt.: CuS Test as usual	Filt.: Chlorides of Fe, Cr and U Boil off H_2S and treat with excess of ammonium carbonate	
	Ppt.: $Fe(OH)_3$, $Cr(OH)_3$ Test as usual	Filt.: $(NH_4)_4UO_2(CO_3)_3$ Test as usual

Procedure III. Treat the residue, left after extraction with dilute hydrochloric acid in Procedure II, with dilute ammonium hydroxide and test the filtrate for silver. If silver is found in the ammoniacal solution test for the following acids, which may have been decomposed by aqua regia with the formation of AgCl.

(a) Treat a portion of the original mixture with Zn and dil. H_2SO_4 and test for Cl, Br, I, CN and CNS as usual.

(b) Test for ferro- and ferricyanides in the sodium carbonate extract of the original mixture for the detection of the acid radicals.

Any residue still left may contain the following compounds:

$BaSO_4$, $SrSO_4$, $Cr_2(SO_4)_3$
CaF_2, ThF_4
Phosphates of Zr, Ti, Th, Ce and Sn
Oxides of Al, Cr, Sn, Sb, Zr, Ti, Th, Ce and Si.

Procedure IV. Fuse the residue with NaOH, Na_2CO_3 and KNO_3 (if coloured) in sufficiently large excess. The changes which will be brought about may be represented conveniently as follows:

$BaSO_4$	→	$BaCO_3$	+	Na_2SO_4		$NaAlO_2$	←			Al_2O_3
$SrSO_4$	→	$SrCO_3$	+	Na_2SO_4		Na_2CrO_4	←			Cr_2O_3
$Cr_2(SO_4)_3$	→			Na_2CrO_4	+ Na_2SO_4	Na_2SnO_3	←			SnO_2
CaF_2	→	$CaCO_3$	+	NaF		Na_3SbO_4	←			Sb_2O_4
ThF_4	→	ThO_2	+					Na_2ZrO_3	←	ZrO_2
$Zr(HPO_4)_2$	→	Na_2ZrO_3	+	Na_3PO_4				Na_2TiO_3 + (TiO_2)	←	TiO_2
$Ti(HPO_4)_2$	→	Na_2TiO_3 + (TiO_2)	+	Na_3PO_4						
								ThO_2	←	ThO_2
$Th(HPO_4)_2$	→	ThO_2	+	Na_3PO_4				CeO_2	←	CeO_2
$Ce(HPO_4)_2$	→	CeO_2	+	Na_3PO_4		Na_2SiO_3	←			SiO_2
$Sn_3(PO_4)_4$	→	Na_2SnO_3	+	Na_3PO_4						

(a) Crush and boil the fused mass with water when all the compounds enclosed within the line will pass into solution. Filter and test the filtrate for

(i) Sulphate, phosphate, fluoride and silicate

(ii) Al, Cr, Sb and Sn

(b) Boil the residue not dissolved by water with conc. HCl filter and test the filtrate for Ba, Sr, Ca, Ti, Zr and Th as follows:

Add NH_4Cl and NH_4OH in excess and filter

Ppt.: Hydroxides of Ti, Zr and Th. Dissolve in conc. nitric acid and test for the three metals by the modified procedure[3].	Filt.: Chlorides of Ba, Sr and Ca. Test as usual.

Procedure V. The insoluble residue obtained after extraction with conc. HCl in *Procedure IV* may still contain ThO_2 and CeO_2. These may be fused with $KHSO_4$ when they will be converted into soluble sulphates. The two metals thus obtained in solution may be tested in the presence of one another by the usual methods.

SUMMARY

A systematic study has been made of inorganic compounds which are difficultly soluble and which may thus be found in the insoluble residue in qualitative analysis.

A scheme has been proposed for the systematic detection of compounds in the insoluble residue obtained in qualitative analysis.

RÉSUMÉ

Une étude systématique a été effectuée sur les composés inorganiques difficilement solubles, pouvant se trouver dans les résidus insolubles de l'analyse qualitative.

Un schéma d'analyse systématique est proposé pour l'identification de ces composés insolubles.

ZUSAMMENFASSUNG

Es wurde eine systematische Untersuchung über die schwerlöslichen anorganischen Verbindungen, welche sich in den Rückständen einer qualitativen Analyse befinden, durchgeführt. Es wird ein Schema einer systematischen Analyse für die Identifikation dieser unlöslichen Verbindungen vorgeschlagen.

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LIMITES DE PH CONCERNANT L'EMPLOI DES „AMPHI-INDICATEURS" EN ALCALI-ACIDIMÉTRIE BIPHASÉE

par

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Dans une communication préliminaire, présentée à l'Académie d'Athènes[1], l'un de nous décrivit les avantages offerts par une nouvelle classe d'indicateurs, permettant le dosage des acides et des bases organiques au sein d'un mélange hétérogène d'eau et d'un solvant non miscible à l'eau. Ces indicateurs spéciaux, (désignés par le symbole *BΔ*) sont des sels obtenus par action de différentes bases organiques (*B*) sur des colorants acides (*Δ*)*, ordinairement utilisés en alcali-acidimétrie. Contrairement aux sels sodiques de ces derniers, les combinaisons en question sont très solubles dans les solvants organiques et peu solubles dans l'eau. Ainsi, si l'on ajoute un indicateur acide à une base aminée dans un système eau-chloroforme et si on agite fortement le mélange, le colorant sera extrait, en principe, par le chloroforme, sous forme de *BΔ* tandis qu'en présence d'un hydroxyde fort, il sera retenu en solution dans l'eau sous sa forme complètement dissociée. La répartition de l'indicateur entre les deux dissolvants dépend donc de la concentration de la phase aqueuse en ions hydrogène. Il est évident que le passage du colorant d'une couche à l'autre, ayant lieu à un pH déterminé, peut servir avantageusement à indiquer la fin d'une titration alcali-acidimétrique. De là les termes *„amphi-indicateur"* et *„amphimétrie"* que nous avons adoptés pour désigner d'une part, les combinaisons du type „*BΔ*" et d'autre part, le procédé volumétrique en présence d'un solvant organique non miscible à l'eau.

Ce nouveau procédé présente un gros avantage sur les méthodes alcali-acidimétriques courantes: l'effet optique servant à indiquer la fin de la titration est exceptionnellement net. En effet, grâce aux conditions spéciales de notre technique, le point de „neutralisation" peut être saisi avec une exactitude extraordinaire, car le passage des amphi-indicateurs de la forme „acide" à la forme „basique" et vice-versa se réalise entre des limites de pH plus rapprochées que celles correspondant au virage normal des indicateurs respectifs. D'autre part, en amphimétrie, les nuances intermédiaires, si génantes quand on opère en milieu homogène, sont exclues, le colorant ne pouvant jamais exister simultanément dans le même solvant sous ses deux états de dissociation. D'ailleurs, cette technique offrant une double indication du point final (coloration d'une phase, décoloration de l'autre), permet la titration d'un acide ou d'une base dans des solutions fortement colorées.

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* *Δείκτης* = indicateur

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Des anomalies plus ou moins sérieuses peuvent naturellement intervenir, si l'on opère en présence d'un amphi-indicateur ne convenant pas. On peut observer, par exemple, un passage plus ou moins graduel de l'indicateur d'un dissolvant à l'autre ou même un saut brusque de celui-ci mais ayant lieu à un stade ne correspondant pas à la fin théorique de la titration. Dans une communication préliminaire, n'ayant pas étudié d'une façon systématique les propriétés des combinaisons $B\Delta$, nous citions qu'en pareils cas l'analyste devrait avoir recours à l'empirisme afin de choisir l'amphi-indicateur s'adaptant plus spécialement à son cas. Entre-temps, ayant complété nos recherches sur ce sujet, nous avons défini les régions de saut d'une centaine de combinaisons $B\Delta$, ainsi que les facteurs influençant les limites des dites régions, tant au point de vue position qu'au point de vue étendue de celles-ci, sur l'échelle des pH.

Dans ce qui suit nous décrivons sommairement la voie expérimentale suivie.

Réactifs

A) *Solutions aqueuses d'indicateurs*: $c = 1 \cdot 10^{-3} M$

1.	Tropéoline OO	(TOO)	P.M. = 375	pK = 2.2
2.	Alizarine S	(NAS)	360	3.4
3.	Méthylorange	(MO)	327	3.5
4.	Bleu de bromophénol	(BPB)	670	3.9
5.	Vert de bromocrésol	(BCG)	798	4.5
6.	Pourpre de bromocrésol	(BCP)	540	6.1
7.	Bleu de bromothymol	(BTB)	624	7.1
8.	Rouge de crésol	(CR)	382	8.0
9.	Bleu de thymol	(TB)	466	8.8
10.	Jaune d'alizarine GG	(AGG)	287	11.0

Les solutions ci-dessus ont été préparées en triturant préalablement dans une petite capsule, à l'aide d'un pistil, les indicateurs peu solubles avec la quantité nécessaire d'hydroxyde de sodium (environ 1.2 ml NaOH 0.1N pour 100 ml de volume final).

B) *Solutions aqueuses d'alcaloïdes*: $c = 1 \cdot 10^{-2} M$

1.	Spartéine, sulfate	(SP)	P.M. = 422.5	pK = 2.24
2.	Atropine, sulfate	(AT)	347.4	4.34
3.	Ephédrine, chlorhydrate	(EP)	201.7	4.50
4.	Procaine, chlorhydrate	(PR)	272.8	5.15
5.	Quinidine, sulfate	(QD)	391.5	5.43
6.	Emétine, chlorhydrate	(EM)	553.6	5.70
7.	Quinine, chlorhydrate	(QN)	396.5	5.95
8.	Codéine, phosphate	(CD)	424.4	6.10
9.	Scopolamine, bromhydrate	(SC)	438.3	6.45
10.	Yohymbine, chlorhydrate	(YO)	390.9	6.50
11.	Strychnine, sulfate	(ST)	428.5	6.80
12.	Pilocarpine, nitrate	(PL)	271.3	7.10
13.	Colchicine, base	(CL)	299.4	12.30

C) *Solutions-tampon, en série échelonnée par degrés de 0.2 pH*

De pH 1.1	à pH 2.2	mélanges	d'HCl-KCl, selon Clark et Lubs
2.2-	5.8	,,	citrate de sodium-HCl/NaOH selon Sörensen
5.8-	8.0	,,	KH_2PO_4-NaOH, selon Clark et Lubs
8.0-	10.0	,,	H_3BO_3-KCl-NaOH, selon Clark et Lubs
10.0-	11.0	,,	borax-Na_2CO_3, d'après Kolthoff et Vleeschhouwer
11.0-	12.0	,,	Na_2HPO_4-NaOH, selon Kolthoff

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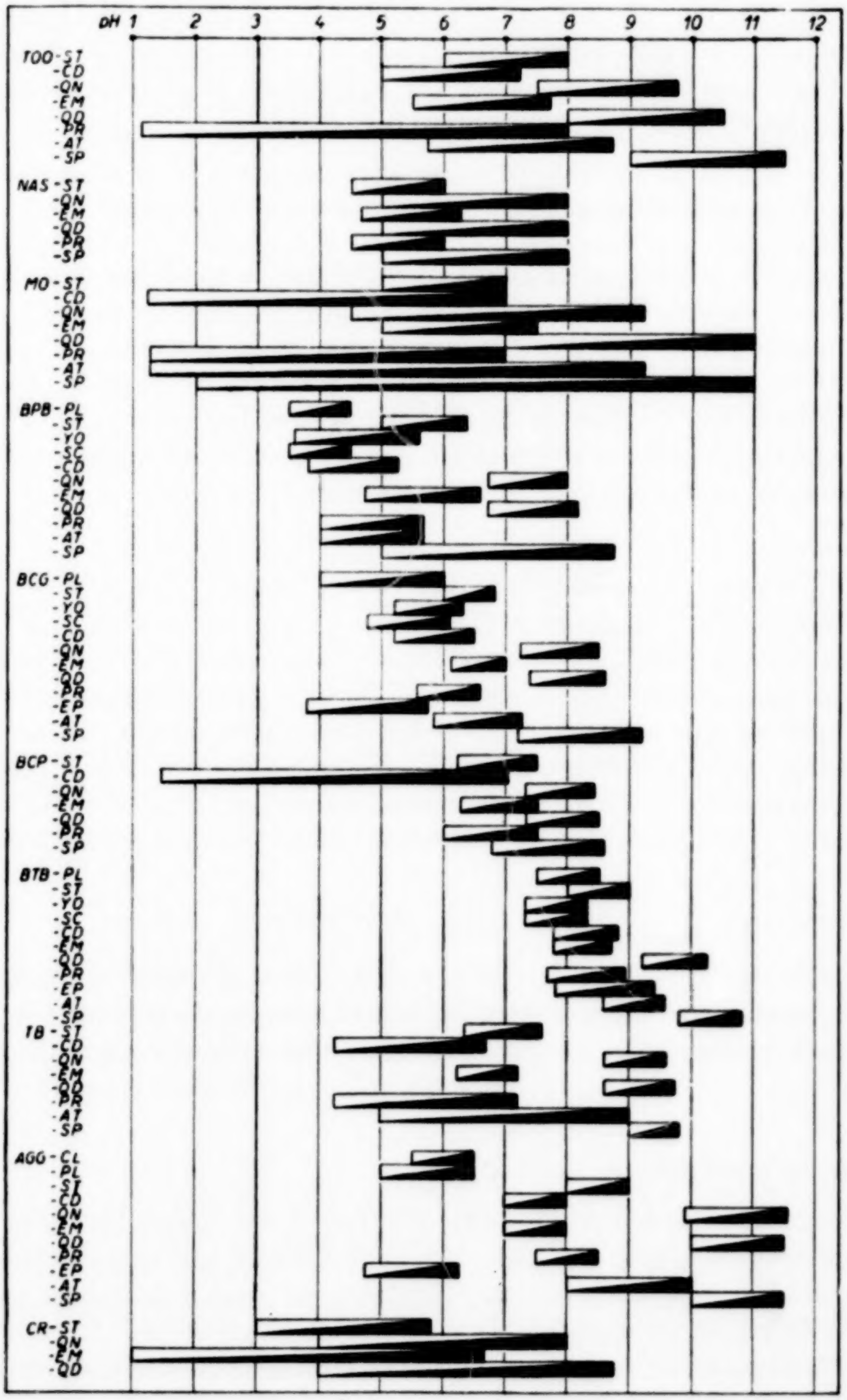
Mode opératoire

On verse dans une éprouvette 0.1 ml de solution d'indicateur, 0.2 ml de solution de base et 4.7 ml de solution tampon; on arrive aux concentrations finales suivantes: $[A] = 2 \cdot 10^{-5}$ et $[B] = 4 \cdot 10^{-4}$. On agite ensuite fortement ce mélange avec 5 ml de chloroforme et, après un court repos, on examine la coloration des deux dissolvants. Tant que l'eau reste incolore, on répète l'essai en ajoutant des tampons à pH progressivement croissants jusqu'à apparition des premières traces d'indicateur dans la phase aqueuse. On note à quel pH l'eau se colore et on continue jusqu'à décoloration complète du solvant organique (en notant le pH).

TABLEAU I



Les résultats de ces expériences sont groupés schématiquement dans le Tableau I, où les rectangles représentent les régions de saut d'un grand nombre de combinaisons $B\Delta$. La limite gauche de chaque rectangle coïncide avec le pH auquel l'eau commence à se colorer, tandis que la limite droite donne le pH où la dernière trace d'indicateur abandonne la phase chloroformique.

Ce tableau nous montre que l'orientation des régions de saut sur l'échelle des pH, quoique théoriquement dépendante des constantes de dissociation des indicateurs et des bases mis en jeu, est néanmoins grandement influencée par la solubilité des combinaisons $B\Delta$. De cette dernière dépend aussi l'intervalle de pH de tout amphi-indicateur. Il est bien évident que pour une application analytique, seules les combinaisons à région de saut étroite présentent un intérêt.

Influence de la concentration de la base

Comme il était à prévoir, nous avons constaté que la solubilité des combinaisons $B\Delta$ dans l'eau décroit, si l'on augmente la concentration de la base organique, ce qui se manifeste par un déplacement de la région du saut vers la droite de l'échelle de pH et par un rapprochement des limites de la région en question. Par exemple, pour les combinaisons, du bleu de bromothymol avec les bases suivantes: quinine, procaïne et émétine, l'indicateur abandonne la couche chloroformique entre les limites ci-dessous lorsqu'on fait croître la concentration de l'alcaloïde:

$\frac{[B]}{[\Delta]}$	*BTB-QN* $[\Delta] = K = 2\cdot10^{-5}$ *Région du saut*	*Etendue en unités pH*	*BTB-PR* $[\Delta] = K = 2\cdot10^{-4}$ *Région du saut*	*Etendue en unités pH*	*BTB-EM* $[\Delta] = K = 3.2\cdot10^{-5}$ *Région du saut*	*Etendue en unités pH*
1	pH 7.4- 9.4	2	pH 5.8- 9.3	3.5	pH 6.6-8.0	1.4
2	8.0- 9.5	1.5	6.8- 9.4	2.6		
5	8.6- 9.7	1.1	7.8- 9.8	2.0	7.0-7.9	0.9
10	8.8- 9.9	1.1	8.0-10.0	2.0	7.7-8.6	0.9
20	9.1-10.1	1.0				
50	9.3-10.1	1.0	8.8-10.0	1.2	8.3-9.2	0.9
100	9.5-10.5	1.0			8.4-9.3	0.9
2500	10.0-11.0*	1.0				

* électrométriquement

On voit donc que l'intervalle en unités de pH se réduit considérablement si $[B]$ dépasse $[\Delta]$, mais qu'à partir d'une certaine concentration de base cette influence devient négligeable.

Influence de la concentration en indicateur

La concentration absolue de l'indicateur influe d'une façon bien plus prononcée sur la grandeur de la région du saut. En diminuant la concentration du colorant, tout en gardant le rapport $[B]$: $[\Delta]$ constant, on réussit à réduire sensiblement l'étendue de la région en question et cela par un déplacement de sa limite droite. Ainsi, le BTB en présence de quinine dans le rapport moléculaire 1:20, quitte la phase chloroformique entre les limites ci-dessous si l'on fait varier $[\Delta]$ comme suit:

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$[\Delta]$	*Région de saut*	*Etendue en unités pH*
$10 \cdot 10^{-5}$	pH 9.0-10.0	1.8
$2 \cdot 10^{-5}$	9.1-10.1	1.0
$1 \cdot 10^{-5}$	9.0- 9.8	0.8
$0.5 \cdot 10^{-5}$	9.0- 9.5	0.5

Influence du rapport des volumes des solvants

Nous avons aussi examiné l'influence éventuelle du rapport des volumes des deux phases liquides sur la région du saut. Nos essais ont démontré qu'on peut faire varier considérablement les volumes respectifs des solvants sans effet remarquable sur la zone de transition. Une déviaton légère est perceptible seulement si l'on réduit beaucoup le volume d'eau. Dans ce cas, pour des raisons purement optiques, le déplacement de la coloration semble avoir lieu à une zone de pH légèrement supérieure. La combinaison BTB-QN par exemple présente les limites suivantes si l'on fait varier comme suit les volumes d'eau (V_{H_2O}) et de chloroforme (V_{CHCl_3}) pour des quantités constantes d'indicateur et de base, soit 0.1 ml de solution $1 \cdot 10^{-3} M$ de bleu de bromothymol et 0.2 ml de solution $1 \cdot 10^{-2} M$ de chlorhydrate de quinine:

V_{H_2O} *(ml)*	V_{CHCl_3} *(ml)*	*Limites du saut*
5	10	pH 9.0-10.0
5	5	9.1-10.1
10	5	9.1-10.1
5	1	9.0-10.2
1	5	9.4-10.4

Un autre point qu'il importait enfin d'examiner, était l'influence éventuelle de la concentration en sels neutres sur la solubilité de différents amphi-indicateurs, c'est à dire savoir si les sels qui se forment au cours d'un titrage amphimétrique, passant en solution dans la phase aqueuse (au lieu des mélanges tampon utilisés lors de nos essais), ont une influence sur les limites déjà trouvées. De nombreuses expériences effectuées dans ce but ont démontré que ces dernières restent pratiquement invariables.

APPLICATIONS ANALYTIQUES

De tout ce qui précède, on peut conclure d'une façon générale, qu'en amphimétrie l'indicateur doit être employé en faible concentration et la base en rapport moléculaire au moins décuple, afin d'atteindre un saut brusque de la coloration à la fin de la titration. Les conditions adoptées sont les suivantes:

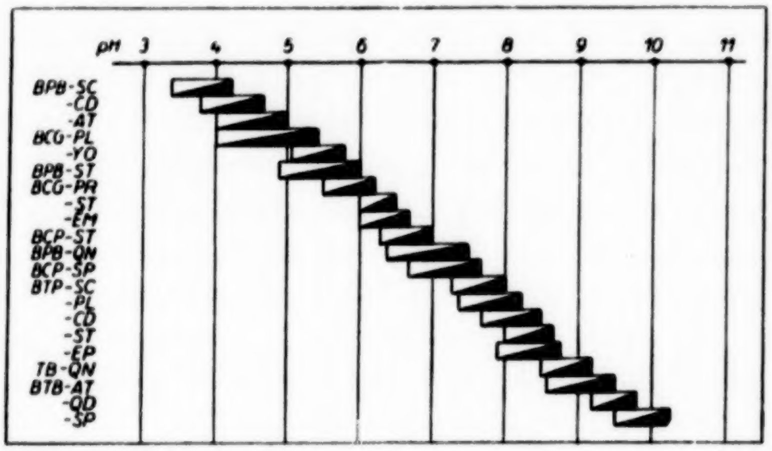
indicateur	$(1 \cdot 10^{-3} M)$	0.1 ml
base organique	$(1 \cdot 10^{-2} M)$	0.2 ml
chloroforme		20 ml
eau (vol. final approx.)		20 ml

($[\Delta]$ finale $= 0.5 \cdot 10^{-5}$, $[B]$ finale $= 1 \cdot 10^{-4}$, $[B] : [\Delta] = 20$)

Dans le Tableau II nous donnons les régions des sauts d'une série de combinaisons $B\Delta$ se prêtant à tout travail amphimétrique si l'on se conforme aux conditions citées. Cette série d'amphi-indicateurs, s'étendant du pH 3.5 au pH 10.3 par degrés ne différant entre eux que de quelques dixièmes de pH, permet à l'analyste de choisir la combinaison $B\Delta$ convenant spécialement à son cas.

Il importe d'ajouter que les limites figurant dans ce tableau peuvent être modifiées à volonté, si l'on tient compte de tout ce qui a été exposé, en faisant varier judicieusement les concentrations des B et Δ choisis.

TABLEAU II



Titration d'acides organiques libres

a) Acides peu solubles dans l'eau: L'amphimétrie permet le dosage des acides organiques difficilement solubles dans l'eau, se dissolvant par contre facilement dans les solvants organiques. En effet, grâce à la présence de choloroforme par exemple, la formation de mélanges agissant comme tampon est grandement limitée, puisque l'acide libre reste pratiquement en solution dans le solvant organique, tandis que le sel de sodium, se formant au cours de la ,,neutralisation'', se dissout quantitativement dans l'eau. La phase aqueuse acquiert, ainsi, dès le début de la titration une concentration en H^+ très voisine du pT (valeur théorique du pH final). Il s'en suit que la limite gauche de la région du saut de l'amphi-indicateur devra correspondre au pT calculé afin d'obtenir le maximum de netteté à la fin de l'opération. Si la valeur de cette limite est inférieure à celle du pT, l'eau se colorera trop vite.

b) Acides solubles dans l'eau: L'amphimétrie ne semble pas présenter, de prime abord, d'avantages sérieux vis-à-vis des méthodes habituelles dans le cas d'acides hydrosolubles, sauf si l'acide à doser se trouve en milieu fortement coloré. Pourtant, même s'il s'agit de solutions incolores, on obtient par ce procédé des résultats plus exacts si l'on opère en présence d'amphi-indicateurs convenables, chose facile si l'on connait la constante de dissociation de l'acide.

Dosage indirect de bases organiques

Il est évident que les conditions diffèrent complètement lorsqu'il s'agit de titrer, par déplacement, un acide fort combiné à une base organique. En pareils cas, on n'aura plus à choisir une combinaison $B\Delta$, mais uniquement le Δ qui serait convenable, puisque la prise contient déjà une base et même en très grand excès, comparativement à la concentration requise pour la formation de l'amphi-indicateur. C'est donc la constante de dissociation et surtout le mode de distribution de la base entre l'eau et le chloroforme qui serviront de guide quant au choix de l'indicateur approprié. Ainsi :

1. Quand il s'agit d'une base très soluble dans le chloroforme et quasi-insoluble dans l'eau, les conditions seront idéales pour l'amphimétrie. Tout indicateur acide donnant avec une telle base une combinaison $B\Delta$, se décomposant au voisinage du pH 7 serait utilisable en principe. L'erreur éventuelle due à un déplacement des limites figurant dans le Tableau II, en raison de la concentration exagérée du système en B (d'ailleurs, erreur négligeable dans la plupart de cas) pourrait, le cas échéant, être évitée en remplaçant vers la fin de la titration l'extrait chloroformique par le solvant pur et en ajoutant une nouvelle quantité d'indicateur.

2. Il en est autrement lorsque la base est très soluble dans l'eau. On conçoit que le choix de l'indicateur dépendra alors principalement de la constante de dissociation de celle-ci. Si la base est sans influence sur la solubilité des colorants compris dans le Tableau II, on ignore sa présence et on procède au choix de l'amphi-indicateur convenable, comme si le système ne contenait pas de base.

Titration d'acides organiques combinés aux bases fortes

Dans notre communication préliminaire, nous disions que l'amphimétrie ne présente pas d'intérêt dans les cas inverses, c'est-à-dire pour la détermination indirecte d'acides organiques par titration de la base forte combinée. Néanmoins, nos expériences ultérieures ont démontré que ce procédé peut offrir entière satisfaction dans plusieurs cas de ce genre.

Evidemment, les conditions sont alors inverses de celles observées jusqu'ici. Ce qui caractérise maintenant la fin de la titration ce n'est plus la décomposition, mais bien la formation de combinaisons du type $B\Delta$, ce qui se manifeste par le passage de la coloration de la phase aqueuse vers le solvant organique.

En consultant le Tableau I on se rend compte que les combinaisons $B\Delta$ les plus sensibles vis-à-vis des ions hydroxyle sont celles du bleu de bromophénol avec les alcaloïdes: pilocarpine, yohimbine, scopolamine et codéine, dont les régions de saut sont situées près du pH 4. Il s'ensuit que seulement les acides très faibles peuvent être titrés indirectement par voie amphimétrique. En supposant qu'on opère sur 1 m/éq de sel (pour un volume final de la phase aqueuse de 20 ml) et que le rapport de distribution de l'acide entre eau et chloroforme soit 1:9, on peut aisément calculer d'après la formule

$$\mathrm{p}K = 2\ \mathrm{pH} + \log c$$

que la constante de dissociation de l'acide ne doit pas dépasser $1 \cdot 10^{-5.7}$. Des acides plus forts peuvent être éventuellement titrés, si leur solubilité dans l'eau est plus faible ou si l'on a soin de remplacer vers la fin de la titration le solvant organique par du chloroforme pur. Dans ce dernier cas on ajoutera naturellement une nouvelle quantité de Δ. La présence d'alcaloïde n'est pas indispensable s'il s'agit de liquides incolores, le virage du bleu de bromophénol au sein de la phase aqueuse étant suffisamment net. D'ailleurs, cette technique a été proposée depuis longtemps par HENVILLE[2] pour l'analyse du benzoate et du salicylate de sodium. Il y a pourtant des cas, notamment quand le sel à doser se trouve en milieu coloré, où l'addition d'une base organique devient inévitable.

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RÉSUMÉ

Les auteurs donnent les intervalles de pH d'un nombre d',,amphi-indicateurs'' (combinaisons d'indicateurs acides avec des alcaloïdes) tout en discutant les avantages offerts par cette nouvelle classe d'indicateurs dans divers cas de titrations alcali-acidimétriques, effectuées au sein d'un système eau-chloroforme.

SUMMARY

The pH intervals of several "amphindicators" (salts of indicator acids with alkaloids) are given. Their advantages and application in alkali-acidimetric titrations, performed in a water-chloroform system, are discussed.

ZUSAMMENFASSUNG

Es wurden die pH-Grenzen einer Reihe von ,,Amphindikatoren'' (Alkaloidsalze der üblichen Farbindikatorsäuren) festgesetzt und die Vorteile sowie die Anwendung derselben bei der Ausführung alkali-acidimetrischer Titrationen in einem Wasser-Chloroform-System diskutiert.

BIBLIOGRAPHIE

[1] G. N. Thomis, *Praktika Akad. Athénon*, 25 (1950) 182.
[2] D. Henville, *Analyst*, 52 (1927) 149.

Reçu le 28 mars 1955

CONTRIBUTION A L'ÉTUDE DE LA STANDARDISATION DES SOLUTIONS ACIDES NORMALES

II. UTILISATION DE L'HYDROGÉNOCARBONATE DE SODIUM COMME SUBSTANCE DE RÉFÉRENCE

par

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INTRODUCTION

Dans un précédent mémoire[1], nous avons résumé nos observations concernant un certain nombre de méthodes classiques de standardisation des solutions acides normales.

Parmi les méthodes par détermination de l'anion de l'acide, la technique au sulfate d'ammonium, d'exécution facile, donne de bons résultats si l'on observe un certain nombre de précautions que nous avons signalées.

Par contre, il est plus difficile de faire un choix parmi les méthodes par détermination du cation H^+, car celles-ci nécessitent une base de référence pouvant être obtenue facilement à un haut degré de pureté. Si l'on emploie comme élément de référence le carbonate neutre de sodium, ainsi que le préconisent de nombreux auteurs, il faut avoir à sa disposition un échantillon purissime que la grande solubilité du produit rend difficile à obtenir, ce qui rend la précision de la méthode tributaire de certaines marques de produits. D'ailleurs, même purissimes, les produits du commerce sont susceptibles de renfermer de petites quantités d'eau, ce qui oblige à les calciner au moment de l'emploi. Dans ces conditions, il était logique de penser que l'on pourrait tout aussi bien utiliser les hydrogénocarbonates de sodium ou de potassium (que leur solubilité réduite permet d'obtenir facilement à l'état pur) et qui, au cours de la calcination, seraient transformés en carbonates neutres correspondants, anhydres, directement utilisables comme élément de référence. Ceci nous a amenés à proposer, pour la détermination du titre exact d'une solution acide, une technique basée sur l'utilisation de l'hydrogénocarbonate de potassium, produit qui se présente sous forme très bien cristallisée et dont les échantillons commerciaux sont habituellement très purs, par suite précisément de leur facilité d'obtention.

La calcination doit cependant être effectuée à des températures comprises entre des limites que nous avons établies. Ces limites ne sont pas un obstacle sur le plan pratique; en effet, elles sont suffisamment larges et le dispositif très simple que nous avons proposé permet d'effectuer la calcination avec toutes les garanties désirables.

Notre attention a toutefois été attirée au cours de nos essais par le fait inattendu suivant:

La température, au-delà de laquelle le carbonate chauffé directement sous cet état est nettement décomposé, est très supérieure à la température au-delà de laquelle le produit de la calcination de l'hydrogénocarbonate ne peut plus être valablement utilisé comme base de référence. Il en résulte que l'on ne peut pas, sans s'entourer de précautions, substituer l'hydrogénocarbonate au carbonate pour obtenir un élément de référence valable pour l'établissement du titre exact des solutions acides étalons. C'est ce point qu'il nous a paru intéressant de confirmer par de nouvelles expériences. Celles-ci ont été réalisées en déterminant, comme nous le précisons dans la partie expérimentale, le "pouvoir titrant" du produit de la calcination du carbonate de sodium et le "pouvoir titrant" du produit de la calcination, à la même température et dans les mêmes conditions, de l'hydrogénocarbonate correspondant.

PARTIE EXPÉRIMENTALE

1. *Calcination*

Des prises d'essai voisines de 2.2 g d'hydrogénocarbonate de sodium* ou de 1.4 g de carbonate de sodium ont été disposées dans une capsule de platine à fond rond d'environ 40 mm de diamètre et chauffées à différentes températures au four électrique. La température peut être considérée comme sensiblement constante pendant toute la durée de l'opération.

Après calcination, la capsule a été abandonnée au refroidissement dans un dessiccateur à acide sulfurique et pesée dans une boîte de verre.

2. *Evaluation du "pouvoir titrant"*

Une solution d'acide sulfurique exactement normale, dont le titre a été vérifié par la méthode au sulfate d'ammonium et celle à l'hydrogénocarbonate de potassium, a été considérée comme étant de titre inconnu.

Ce titre a alors été déterminé en utilisant successivement comme base de référence les produits de la calcination, à différentes températures et pendant le même temps, du carbonate neutre de sodium et du bicarbonate de sodium. On admet dans le calcul que, quel que soit le poids trouvé, le produit de la calcination est constitué exclusivement par du carbonate de sodium pur et anhydre. Il en résulte que si tous les produits de calcination étaient vraiment du carbonate de sodium pur et anhydre, ils auraient tous le "pouvoir titrant" théorique du carbonate neutre de sodium anhydre et le titre trouvé pour la solution dosée serait dans tous les cas exactement 1.000*N*, aux erreurs d'expérience près.

La technique utilisée pour le dosage a été celle décrite précédemment[1]. L'utilisation d'un indicateur** virant en zone acide permet d'éviter l'élimination de l'acide carbonique présent.

Le titre de la solution dosée est donné par la relation:

$$\text{Titre (en normalité)} = \frac{1000\,p}{53 \times n}$$

---

* Nous avons utilisé des échantillons puriss. Merck.

** Certaines solutions de cet indicateur, préparées comme il a été indiqué dans le précédent mémoire, ont laissé apparaître à la longue un léger précipité. Des solutions très stables peuvent être obtenues de la façon suivante:

Méthylorange	0.025 g
Vert de bromocrésol	0.125 g
Ethanol à 50 %	100 ml

Triturer au mortier jusqu'à complète dissolution. Filtrer. Pour chaque dosage utiliser 4 gouttes de cette solution.

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dans laquelle:

p (en g) = poids du produit obtenu après calcination

n (en ml) = volume total de la solution acide nécessaire pour obtenir le virage de l'indicateur à la teinte champagne.

3. *Résultats obtenus*

Les résultats obtenus sont représentés sur les Figures 1 et 2.

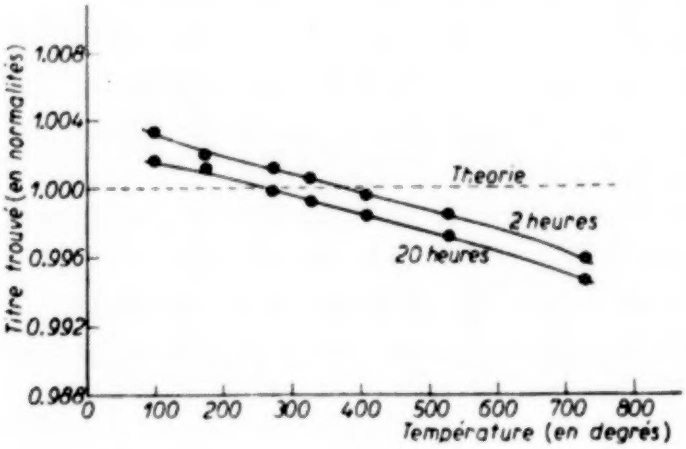

Fig. 1. Variations du "pouvoir titrant", en fonction de la température de chauffage de l'hydrogénocarbonate de sodium.

Abcisses = Température de chauffage de l'hydrogénocarbonate de sodium.
Ordonnées = Résultats du dosage (en normalités) d'une solution d'acide sulfurique N.
Durée du chauffage = 2 heures et 20 heures.

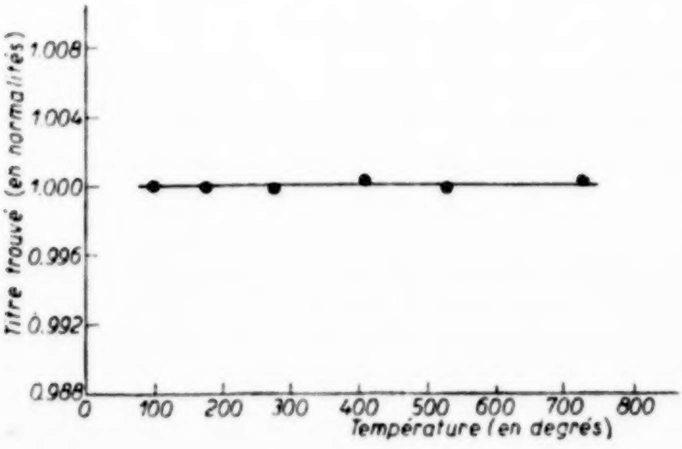

Fig. 2. Variations du "pouvoir titrant", en fonction de la température de chauffage, du carbonate neutre de sodium.

Abcisses = Température de chauffage du carbonate de sodium.
Ordonnées = Résultats du dosage (en normalités) d'une solution d'acide sulfurique N.
Durée du chauffage = 2 heures.

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DISCUSSION DES RÉSULTATS

1. *Variations du pouvoir titrant en fonction de la température de chauffage de l'hydrogénocarbonate de sodium*

L'examen de la Fig. 1 montre que le "pouvoir titrant" du produit de la calcination de l'hydrogénocarbonate de sodium, dans les conditions de nos expériences, varie suivant la température de chauffage et, plus faiblement, avec la durée de ce chauffage. Nous avions d'ailleurs remarqué antérieurement[1]* que la perte de poids observée au cours de la calcination ne correspond à la perte de poids théorique (c'est-à-dire à la transformation quantitative exacte de l'hydrogénocarbonate en carbonate) que pour une zone de température assez étroite.

D'un autre côté, il est à remarquer que la courbe représentant les variations du „pouvoir titrant" du produit de la calcination pendant 2 heures de l'hydrogénocarbonate de sodium diffère très nettement de celle obtenue dans les mêmes conditions dans le cas de l'hydrogénocarbonate de potassium[1]. Cette dernière comportait en effet un palier très net pour une température de chauffage comprise entre 250° et 350°. Il en résulte sur le plan pratique que l'emploi de l'hydrogénocarbonate de potassium est préférable à celui de sodium pour l'obtention d'une base de référence en acidimétrie, et ceci en dehors du fait que le sel courant du commerce est plus pur que celui de sodium**.

2. *Comparaison entre le pouvoir titrant du produit de la calcination du bicarbonate de sodium et celui de la calcination du carbonate neutre de sodium*

Mais si, dans les conditions de nos expériences, le pouvoir titrant du produit de la calcination du bicarbonate de sodium varie suivant la température de chauffage, il n'en est pas de même dans le cas du produit de la calcination du carbonate neutre de sodium. La Fig. 2 montre que pour ce dernier le "pouvoir titrant" est rigoureusement constant ainsi que d'ailleurs l'avaient déjà montré DUPUIS ET DUVAL[2].

La durée du chauffage ne semble pas non plus avoir d'influence sur le pouvoir titrant car ce pouvoir titrant a été trouvé exactement identique pour une durée de chauffage de 20 heures au lieu de 2 heures.***

Comme la calcination de l'hydrogénocarbonate et celle du carbonate de sodium ont été conduites de façon rigoureusement identique, il s'ensuit que le produit de la calcination de l'hydrogénocarbonate n'est pas identique à celui de la calcination du carbonate neutre correspondant, tout au moins dans les conditions de nos essais.

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* Une erreur de dactylographie, dont nous nous excusons, a fait reproduire (Tableau I, p. 15) un chiffre erronné. Au lieu de 71.91 il fallait lire 51.91.

** C'est ainsi qu'il est d'usage courant dans notre laboratoire d'utiliser de préférence le sel de potassium toutes les fois qu'il est nécessaire de laisser en contact de l'iode en milieu bicarbonaté au cours de déterminations analytiques fines. L'usage du sel de sodium de pureté courante, dans ce cas, amène des consommations anormales d'iode. Ces erreurs doivent être attribuées à une impureté du bicarbonate de sodium puisqu'elles disparaissent si l'on soumet ce produit à un lavage préalable.

*** Nous noterons cependant qu'un certain nombre d'auteurs ont observé, mais dans des conditions expérimentales différentes des nôtres (courant d'azote, avec ou sans vapeur d'eau), une nette décomposition du carbonate de sodium à des températures peu élevées. C'est ainsi que tout récemment JANJIĆ, BRINER ET PAILLARD[4] ont observé une décomposition dès 100° en opérant sous courant d'azote en présence de vapeur d'eau.

Sur le plan pratique, on ne peut donc pas, sans risque d'erreurs, utiliser indifféremment ces produits comme base de référence en acidimétrie.

Ces conclusions s'accordent avec celles de WALDBAUER, McCANN ET TULEEN[3] qui ont montré que le carbonate de sodium obtenu par calcination du bicarbonate contient des impuretés que les auteurs pensent être de l'oxyde de sodium. Ils établissent que ces impuretés peuvent être éliminées par lavage à l'alcool et que le produit ainsi obtenu peut alors être chauffé sans altération de son pouvoir titrant.

Ces mêmes conclusions s'accordent également, mais bien à l'insu de l'auteur, avec l'expérience effectuée par LASSIEUR[5], dans des conditions opératoires un peu différentes des nôtres.

A condition de laisser de côté les calculs et le raisonnement qui nous paraissent erronés, cette expérience s'établit comme suit:

3.5 g environ de bicarbonate de sodium sont chauffés à 200° jusqu'à poids constant. Le produit obtenu pèse 2.2225 g. Le poids de ce même produit, après chauffage à 600°, est de 2.2165 g. La quantité de HCl *N* versée pour le titrage = 41.9 ml.

Avec le premier produit la quantité de HCl versée devrait être évidemment la même soit 41.9 ml et le titre trouvé pour la solution aurait été de $\frac{1000 \cdot 2.2225}{53 \cdot 41.9} = 1.0014N$; dans le second cas le titre est: $\frac{1000 \cdot 2.2165}{53 \cdot 41.9} = 0.9988N$.

Il s'ensuit entre les deux résultats une différence de 2.6 p. 1000 dans le titre de la solution acide dosée. Cette différence est du même ordre de grandeur que celles de la Fig. 1.

Nous remercions M. le Professeur FLEURY pour l'intérêt qu'il a bien voulu prendre à ce travail.

RÉSUMÉ

Les auteurs montrent expérimentalement que l'emploi du produit brut de la calcination de l'hydrogénocarbonate de sodium comme substance de référence en acidimétrie est à déconseiller.

SUMMARY

Experiments have shown that it is not advisable to use the crude product of the calcination of sodium bicarbonate as a standardization substance in acidimetry.

ZUSAMMENFASSUNG

Die Autoren zeigen experimentell, dass von der Anwendung des rohen Kalzinationsproduktes von Natriumbikarbonat als Bezugssubstanz bei der Säure-Basen-Titration abzuraten ist.

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SIMPLE INSTRUMENT FOR TITRIMETRY WITHOUT VISUAL INDICATORS. GASOMETRIC TITRATIONS

XI. DICHROMATOMETRY

by

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The title "gasometric titrations" gives the impression that only systems of sample and titrant which release a gas can be analysed directly by this method. The error of this assumption was shown by examples given in a previous paper[1], and it will be demonstrated again in the present one.

The disadvantage of potassium dichromate as a volumetric oxidizing agent is that the indicators used with it are rather unsatisfactory[2] owing to its low oxidation-reduction potential, which limits the choice of the indicator, and to the fact that the color change at the end-point is obscured somewhat by the deep green or violet color of the chromic ion.

The difficulty of the indicator can, of course, be avoided by potentiometric titration[2], but the gasometric titration procedure outlined below is also independent of the color of the sample and has the added advantage that it can be performed with the aid of the very simple and inexpensive instrument described previously[1].

Reagents

Potassium dichromate, 0.5 and 0.1N solutions.
Sulfuric acid, 6N solution.
Hydrazine sulfate, 0.1M solution.
Ferrous ammonium sulfate solutions.
Stannous chloride solutions.

Procedure

Transfer 5.00 ml of the sample solution, which contains ferrous (or stannous) ions, to the titration flask, and add 5 ml of the sulfuric acid solution and sufficient hydrazine sulfate (approx. 5 ml of 0.1M solution for 0.1N titrant). Connect the flask with the buret which contains the titrant. Put the magnetic stirrer in motion and close the stopper on top of the buret. Titrate until the end-point has just been passed somewhat (gas evolution ensues), read the volume of titrant added, wait until the gas has been evolved and read the volume of water displaced from the inverted buret. Continue to add the titrant in definite increments (*e.g.* 1 ml). At fixed intervals (e.g. 2 minutes) after each addition, read the volume of water displaced. Three such additions are sufficient. Plot the volume of titrant against the volume of water displaced. Extend the straight-line portion of the curve to intersect the abscissa. The intersection marks the end-point.

Precision and accuracy

Tables I and II show that the observations made in the previous paper of this series are valid.

Taking into consideration exclusively the construction of the graph, the steeper the titration curve (and hence the more concentrated the titrant) the better will be the precision of the analysis.

TABLE I

TITRATION OF FERROUS AMMONIUM SULFATE SOLUTION WITH POTASSIUM DICHROMATE SOLUTION

ml Fe^{+2} solution taken	*ml 0.5N $K_2Cr_2O_7$ consumed*		
	gasometric titration	external indicator method	Δ %
5.00	1.62		
5.00	1.64		
5.00	1.63		
	mean 1.63	mean 1.63	0.00
	ml 0.1N $K_2Cr_2O_7$ consumed		
	gasometric titration	external indicator method	Δ %
5.00	5.16		
5.00	5.16		
	mean 5.16	mean 5.17	−0.19
5.00	5.04		
5.00	5.06		
	mean 5.05	mean 5.05	0.00
5.00	3.20		
5.00	3.18		
5.00	3.18		
5.00	3.25		
	mean 3.20	mean 3.18	+0.63

TABLE II

TITRATION OF STANNOUS CHLORIDE SOLUTION WITH POTASSIUM DICHROMATE SOLUTION

ml Sn^{+2} solution taken	*ml 0.5N $K_2Cr_2O_7$ consumed*		
	gasometric titration	indicator ferroin	Δ %
5.00	4.78		
5.00	4.74		
	mean 4.76	mean 4.77	−0.21
	ml 0.1N $K_2Cr_2O_7$ consumed		
	gasometric titration	indicator ferroin	Δ %
5.00	5.20		
5.00	5.16		
5.00	5.20		
	mean 5.19	mean 5.14	+0.97

Interferences

A number of anionic and cationic oxidants are capable of reacting with hydrazine in acid solution. However, either the presence of such substances is incompatible with the presence of ferrous ion in the sample solution, or the reactions are too slow at room temperature in acid solution — as in the case of ferric ion[3] — to cause interference.

DISCUSSION

An evident solution for the case in which sample and reagent do not release directly a gas, is the use of a titrant which does release one with excess reagent. Nevertheless it is often possible to use a direct gasometric titration procedure by adding to the sample solution a substance which will release a gas with the titrant. There are several requirements to be fulfilled by such a substance: (1) it must not react with the sample under the conditions of the analysis; (2) its reaction velocity with the titrant must not be greater than that of the sample itself. In fact a substance can be considered ideally suited if its reaction with the titrant starts only when all, or nearly all, of the sample has reacted. This condition is by no means vital, and even if sample and substance react at approximately the same rate with the titrant, the substance can serve as gasometric indicator. In this case it must be added in such a quantity that when all the sample has reacted, the titrant still encounters sufficient indicator to allow the construction of the straight-line portion of the titration curve.

The reaction between hydrazine and dichromate

$$3N_2H_4.H^+ + 2Cr_2O_7^{-2} + 13H^+ \rightarrow 3N_2 + 4Cr^{+3} + 14H_2O$$

is a limiting reaction which can be approached but not realized[4]. Nevertheless, for the purpose of the present work it is sufficient that a straight-line titration curve results as long as a regular excess of hydrazine is present.

If, as in organic oxidation methods, an excess of dichromate must be used, an excess of ferrous solution of known concentration can be added and back-titrated with dichromate solution as shown above.

Since the whole quantity of titrant needed to react with the sample is added very rapidly and the solution is covered near the end-point by a layer of nitrogen, errors due to aerial oxidation of the sample are minimized in the present method. Preliminary experiments indicated the possibility of titrating titanous salts by the procedure described in this paper.

ACKNOWLEDGEMENT

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SUMMARY

Even ions which do not release gases with a certain titrant can be determined by direct gasometric titration. To achieve this end, a substance which liberates a gas with the titrant, must be added to the sample solution. The end-point of the main reaction can be read from the gasometric titration curve of this indicator substance.

This principle is applied in the present paper to the titration of ferrous and stannous ions by potassium dichromate. Hydrazine sulfate serves as indicator. The results are comparable in precision and accuracy to the values obtained by the conventional visual end-point titrations.

RÉSUMÉ

Même les ions qui ne libèrent pas des gaz avec le réactif titrant peuvent être dosés par titration gazométrique directe. Pour cela, on introduit une autre substance libérant un gaz avec le réactif. Le point final de la réaction principale peut être déterminé à partir de la courbe de titration

gazométrique de cette substance-indicateur. Ce procédé a été appliqué ici à la titration des ions fer(II) et étain(II) par le dichromate de potassium; le sulfate d'hydrazine sert d'indicateur. Les résultats sont comparables comme précision et exactitude aux valeurs obtenues par les méthodes usuelles.

ZUSAMMENFASSUNG

Selbst diejenigen Ionen, welche mit dem zur Titration verwendeten Reagenz kein Gas bilden, können durch direkte gasometrische Titration bestimmt werden. Man gibt noch eine andere Substanz dazu, welche mit dem Reagenz ein Gas freigibt. Der Endpunkt dieser Hauptreaktion, kann an Hand der gasometrischen Titrationskurve dieser Indikator-Substanz bestimmt werden. Dieser Vorgang wurde hier für die Titration der Eisen(II) und Zinn(II)-Ionen mit Kaliumbichromat angewandt. Das Hydrazinsulfat dient als Indikator. Die Resultate sind in Bezug auf Präzision und Exaktheit mit den Werten der üblichen Methoden vergleichbar.

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STUDY OF INTERFERENCES IN THE IODOMETRY OF TIN ITS APPLICATION TO ORE ANALYSIS

by

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Owing to the great interest that our country and particularly this laboratory has in the analysis of tin ores, we decided some time ago to initiate a systematic study of the possible interferences in that analysis.

It may be said that this study began with a previous work of ours[1], in which a critical study was made of several methods for the determination of tin in its ores. In that work we arrived at the conclusion that the best method now in use for the determination of tin is the iodate method, which is almost universally followed. Furthermore, in that work we indicated the interferences cited up to that time in the technical literature, and we made a detailed study of the most important interference in this country, namely that of tungsten.

The paper now presented is related to the interference of molybdenum, and in further papers we will describe our examinations of other interferences cited, and of some not yet cited in the literature.

INTERFERENCE OF MOLYBDENUM

I. INTRODUCTION

The occurrence of tin and molybdenum simultaneously in some natural products which we analysed, made us decide to consult the literature on the interference of molybdenum in tin determination. We found no important work on the matter, but only a few vague references.

MELLOR AND THOMPSON[2] said that in the titration of tin after reduction with nickel, the presence of molybdenum does not interfere, but the brown colour of the solution makes the observation of the end-point difficult or even impossible. Nevertheless, WEINIG AND SCHODER[3] found that the presence of elements partially or totally reduced by nickel in strong acid solution and oxidized afterwards by iodine, causes high results for tin. Molybdenum and vanadium are in the above condition, and these elements may occasionally be present in tin ores.

It is obvious that although both books cited are classics, the opinions about this matter are conflicting.

In another classic work, that of HILLEBRAND AND LUNDELL[4], it is said that in the determination of tin, when lead is used as reductor, the presence of molybdenum, chromium or vanadium leads to high results because those elements are reduced and consume iodine during the titration.

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CHARLOT[5] when describing the determination of tin by volumetry with bromate, says: "Mo (VI) is reduced by zinc, and slightly by antimony, consuming bromate during the titration of tin".

Finally, in a recent paper by DUPRAW[6], emphasis is placed on the problem of the determination of tin in titanium alloys containing molybdenum. The author concludes that molybdenum interferes in an erratic manner. He obtains an almost total elimination of the interference by previous oxidation with H_2O_2 (30%) before the final titration. However, slightly high results are always obtained which are supposed to be due to the slight oxidation of the Mo(V) by the iodate.

The references we have just cited, the only ones we found, are concerned with reductions by nickel, zinc and antimony, and titrations with iodate and bromate. However, as the method we used was the reduction with aluminium followed by titration with iodate, which was adopted after a careful examination of all the existing methods, the study of the interference of molybdenum in this method became necessary.

2. STUDY OF PURE SOLUTIONS OF TIN AND MOLYBDENUM

Reagents

Tin "Baker"
Molybdic acid "Baker & Adamson" (99.5% MoO_3)
Aluminium (in sheets) "Merck"
Iron powder "B.D.H."
Hydrochloric acid (d = 1.19) "Merck"
Sodium hydroxide "Merck"
Iodine "May & Baker"
Potassium iodide "Riedel"
Soluble starch "Riedel" (2% solution)

All the reagents were analytical grade.

Solutions used

Tin solutions were prepared by dissolving *ca.* 7 g of tin in 100 ml of HCl (d = 1.19) in a 1000 ml volumetric flask and then making it up to the mark with distilled water.

Solution I - 7.2036 g of tin
Solution II - 7.2196 g of tin

Molybdenum solution was prepared by dissolving 3.0149 g of dried MoO_3 in 50 ml of water containing 10 g of NaOH, warming slightly to facilitate solution. After cooling, it was diluted to 1000 ml, giving a solution in which 1 ml = 0.002 g of Mo.

Iodate-iodide solution was prepared by the same technique already indicated in a former paper[1], giving a solution approximately 0.15*N*, containing 56 g of KI per litre.

Experimental design

We usually establish a previous design of each investigation in order for it to be possible, when necessary, to apply statistical analysis to the results obtained. Of course statistics are not always needed, but when they are, much time is saved by the use of such a design.

In Table I the established design is summarized using the symbol S_{Sn} for "tin solution" and S_{Mo} for "molybdenum solution".

Experiments 1, 2, 3 and 4 were prepared by adding to the two solutions of tin and molybdenum 75 ml of HCl and enough water to make up 200 ml; the final solution must be 40% (v/v) in HCl.

For the same reason, in experiments 5, 6, 7 and 8, 77.5 ml of HCl were added; in the experiments 9, 10, 11 and 12, 79 ml, and in the experiments 13, 14, 15 and 16, 80 ml of HCl were added. In each case the final volume of 200 ml was made up by addition of water.

All the experiments were conducted in duplicate or sometimes even in triplicate.

TABLE I

S_{Sn} S_{Mo}	*50 ml*	*25 ml*	*10 ml*	*0 ml*
50 ml	1	5	9	13
25 ml	2	6	10	14
10 ml	3	7	11	15
0 ml	4	8	12	16

Procedure

Each of the solutions already indicated was prepared in a 500 ml conical flask. Then 1.5 g of aluminium were added, the flask was stoppered with a cork pierced by a glass tube dipped in a saturated solution of $NaHCO_3$. Once the aluminium is dissolved (20 to 30 minutes) the flask must boil gently in order to dissolve the tin sponge. The flask is immediately cooled in cold water, keeping the tube always dipped in the $NaHCO_3$ solution. After total cooling the cork is removed, a small piece of $CaCO_3$ and 2 ml of starch solution are added, and the solution is rapidly titrated with KIO_3 - KI solution.

Results

For easier comparison the results were grouped together in Table II.

TABLE II

1	35.90 ml 36.70 ml	5	15.20 ml 13.65 ml 12.80 ml	9	5.75 ml 5.10 ml 5.60 ml	13	0.05 ml 0.20 ml
2	42.00 ml 39.70 ml	6	19.75 ml 19.20 ml 18.80 ml	10	8.10 ml 8.60 ml 8.20 ml	14	0.05 ml 0.15 ml
3	43.20 ml 43.20 ml	7	21.60 ml 21.60 ml	11	8.60 ml 8.60 ml 8.60 ml	15	0.05 ml 0.10 ml
4	42.80 ml 42.95 ml 42.90 ml	8	21.40 ml 21.50 ml 21.45 ml	12	8.35 ml 8.45 ml 8.45 ml	16	0.05 ml 0.05 ml

Observations on the experiments

(a) In experiments 1 to 12 the first figure of each group was obtained by slow addition of the iodate with slight stirring, as we did not know the end-point. The second and third experiments were performed by the addition of 95% of the total volume of iodate all at once, and without stirring, and then drop by drop until the end-point.

(b) The first experiments of groups 13 to 16 were obtained using as indicator 2 ml of 2% starch solution containing 2.5% KI. In the second ones the indicator was only 2 ml of 2% aqueous starch solution.

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(c) The experiments of the first row presented a deep pink colour after reduction by the aluminium, those of the second row showed a pinkish yellow colour, those of the third row were light yellow and those of the fourth row were colourless.

(d) It was observed that in all the experiments containing molybdenum, when the solution is exposed to the air after the end-point has been reached, the blue final colour faded slowly. If a drop of iodate was then added the blue colour returned, but afterwards it faded again.

Conclusions

As the results are so dissimilar we may, even without using statistical analysis, arrive at the following conclusions:

1. A marked interference was observed in the tin determination when molybdenum is present. This interference consists of a slight increase of the iodate consumption when the amount of molybdenum is small (*ca.* 0.02 g), and a marked decrease of the consumption with greater amounts of molybdenum.
2. The above cited consumption decrease is greater or less according to the amount of molybdenum present.
3. The results obtained in the presence of great amounts of molybdenum (0.05 to 0.10 g) are low and fluctuating and seem to be even lower when the titration is made quickly.
4. The results of the last column show that in the absence of tin, the molybdenum does not interfere, *i.e.*, it does not consume iodate.
5. The observation (d) of the preceding section shows that there is probably a slight oxidation of the molybdenum by the iodate, which would explain the slow fading of the blue colour.

3. STUDY OF SOLUTIONS OF TIN AND MOLYBDENUM CONTAINING IRON

Since in the determination of tin in natural products there is always some iron present, either from the crucible in which the disaggregation took place, or from the treatment with "ferrum reductum" which is made to eliminate some existing interferences, we decided to repeat some of the former experiments after previous addition of iron to the solution.

Design of experiments

In each case the solution resulting from the addition of tin and molybdenum solutions, was made up to 100 ml with distilled water.

TABLE III

S_{Sn} / S_{Mo}	*50 ml*	*10 ml*
50 ml	A	E
25 ml	B	F
10 ml	C	G
0 ml	D	H

Experimental

To the above-mentioned 100 ml are added 50 ml HCl and 50 ml H_2O, in a 400 ml beaker. After the addition of 1.5 g of "ferrum reductum", the solution is heated in a water-bath until the iron is completely dissolved. Then 0.2 g more iron is added and the filtration is performed into a 500 ml conical flask. The filter is washed with 10% hydrochloric acid (twice in the beaker and 4 times in the filter). A piece of pure aluminium (1.5 g) is then added to the solution in the flask which is stoppered with a cork as already described, and the dissolution is completed without further warming. The flask is then opened, and more HCl (50 ml) and a fragment of aluminium are added (in order to counteract the action of any small amount of air which could have entered, or traces of free chlorine from the HCl). After the flask is again stoppered, it is boiled until the tin sponge is completely dissolved, then it is removed, cooled and the titration is performed as already described.

Results

The colours of the reduced solutions are more or less the same as those indicated in the former chapter, being only slightly modified by the green colour of the ferrous ion.

TABLE IV

A	46.90 ml	E	8.60 ml
	46.90 ml		8.60 ml
B	46.90 ml	F	8.60 ml
	46.80 ml		8.60 ml
C	46.80 ml	G	8.60 ml
	46.80 ml		8.60 ml
D	46.70 ml	H	8.50 ml
	46.60 ml		8.50 ml

Conclusions

The results obtained allow the following conclusions:

1. Whenever a ferrous salt is present in a tin-molybdenum solution, the interference of the latter in the titration of tin is shown by a slight increase of iodate consumption (0.10 to 0.30 ml).
2. Increase seems to be greater when greater amounts of tin are present.
3. When the amount of tin is higher, the increase in the consumption seems to be proportional to the amount of molybdenum.
4. When the amount of tin present is small, no increase in iodate consumption is observed.

4. DISCUSSION

In order to give a more logical sequence to the discussion of the results, we shall examine the following cases seperately: reduction of Mo, Mo-Sn and Mo-Sn-Fe solutions by aluminium.

Reduction of molybdenum solutions by aluminium

Though Charlot (*loc. cit.*) has cited several reductions of molybdenum by metals in acid medium, he said nothing about aluminium. However, in a recent paper by Riegel and Schwartz[7], a very detailed study of the reduction of molybdenum by aluminium in acid medium, is made. The authors said that nothing more than a brief reference by Willard and Furman[8] was found on this subject. According to Riegel and Schwartz, a hydrochloric ($2M$) or sulphuric ($1.25M$) solution of molybdenum when treated by an excess of aluminium (sheet or powder), in nitrogen atmosphere, turns from colourless to orange [Mo(VI)→ Mo(V)], and afterwards to green [Mo(V)→ Mo(III)]. As we had not reached exactly the same results, since experiments 13 to 16 of Table II gave pinkish orange solutions indicating Mo(V), we decided to carry out some supplementary experiments in conditions more similar to those of the cited authors. In fact the acidity utilized by us in our experiments was 4*M* and the aluminium was in wire form.

We carried out six experiments all of them containing 0.1 g of Mo and a total volume of 200 ml, the reduction being effected with 2 g of Al.

TABLE V

Experiment	*Conditions*	*Final colour*
1	HCl (4*M*)-Al (sheet)	Orange pink
2	HCl (2*M*)-Al (sheet)	Deep orange
3	H_2SO_4 (1.25*M*)-Al (sheet)	Dark brown (even after 8 hours of boiling, the Al was not completely dissolved)
4	HCl (4*M*)-Al (powder)	Orange
5	HCl (2*M*)-Al (powder)	Deep orange (in the beginning the solution was green, changing to orange during the boiling)
6	H_2SO_4 (1.25*M*)-Al (powder)	Dark green

Experiments 1 and 4 when titrated with iodate consumed 2 drops, and experiments 2 and 5 consumed *ca.* 0.6 ml.

So far, from the results obtained, we may conclude that in 4*M* HCl it is not possible to get Mo(III), but only Mo(V). Working under the conditions mentioned above and without nitrogen atmosphere, in 2*M* HCl, we get a mixture of Mo(III) and Mo(V) as is demonstrated by the dark colours of the solutions as well as by the titration results obtained. In sulphuric medium the obtaining and conservation of Mo(III) appears to be easier.

This is our interpretation of the apparent discrepancy between our results and those of RIEGEL AND SCHWARTZ.

The results of experiments 13 to 15 of Table II are easily understandable: — In those experiments, as the medium is 4*M* HCl, Mo(VI) was reduced by aluminium to Mo(V) which, according to DUPRAW (*loc. cit.*) and our own observations, is slowly oxidized by KIO_3, this oxidation being dependent on the molybdenum concentration and on the rate of titration. This is the reason why, although the titration rates were similar, the figures obtained were, respectively, 0.20, 0.15 and 0.10 ml of KIO_3.

Reduction of Sn-Mo solutions by aluminium

A recent paper by CROUTHAMEL AND JOHNSON[9] on the spectrophotometry of molybdenum, has enabled us to find a satisfactory explanation for the results obtained.

According to those authors, when an excess of $SnCl_2$ is used, the following reaction is observed:

$$\mathrm{Mo(VI)} + \mathrm{Sn(II)} \xrightarrow{\text{rapid}} \mathrm{Mo(IV)} + \mathrm{Sn(IV)} \qquad (1)$$

immediately followed by the dismutation of Mo(IV):

$$2\ \mathrm{Mo(IV)} \rightleftarrows \mathrm{Mo(V)} + \mathrm{Mo(III)} \tag{2}$$

In chloride medium ($> 3M$ hydrochloric acid) the reactions (1) and (2) are followed by

$$\mathrm{Mo(V)} + \mathrm{Sn(II)} \rightleftarrows \mathrm{Mo(III)}\ \text{or}\ \mathrm{Mo(IV)} + \mathrm{Sn(IV)} \tag{3}$$

In our case (reductions by aluminium) Mo(VI) would be reduced to Mo(V), but as all the tin present was also reduced to Sn(II), reaction (3) would probably take place, immediately followed by reaction (2). Consequently the final solution would have the molybdenum as Mo(V) and Mo(III), Mo(V) probably dominating judging from the solution colour.

As the reduction of Mo(V) to Mo(III) was effected by Sn(II), which consequently was transformed into Sn(IV), when we titrated the final solution the iodate consumption was less than when molybdenum is not present.

Although equilibrium (3) is displaced to the left due to the disappearance of Sn(II) during the titration, we must bear in mind that the high concentration of Mo(V) impedes that displacement, preventing the total amount of Sn(IV) from being transformed into Sn(II).

Whenever the titration was performed very rapidly, a smaller consumption of iodate was observed. This fact could be attributed to the low speed of reaction (3) from right to left.

As one would expect, it is observed that the higher the concentrations of Sn and Mo (experiments 1, 2, 5 and 6) the greater are the differences obtained. However, in experiments 9 and 10, notwithstanding the high Mo content, the differences were found to be fewer than in the former ones, which is a proof of the great importance of Sn(II) concentration.

It is curious that when there is a low content of Mo (experiments 3, 7 and 11) a slight increase of theoretical iodate consumption is observed, independent of titration speed. The well-known slight iodate consumption of Mo(V), as well as the slow rate of reaction (3) for low Mo contents, would justify that slight increase of iodate consumption.

Reduction of Sn-Mo-Fe solutions by aluminium

It was again the above-mentioned paper by CROUTHAMEL AND JOHNSON that enabled us to attempt an explanation of the fact observed by us that when iron is present in the solution the anomalies above cited were not observed. In these experiments, as is summarized in Table IV, only that slight increase observed formerly in experiments with small amounts of Mo was noticed.

According to those authors' conclusions, the presence of Fe or Cu in the solution catalyzes the transformation Mo(III) → Mo(V). Consequently, in such ferrous solutions as ours, Mo(III) cannot exist. Assuming that the presence of Mo(III) is, according to our opinion, the cause of the observed anomalies, if our interpretation is correct we should not have consumed any additional amount of iodate, as was actually the case.

5. INFLUENCE OF Mo IN THE TIN DETERMINATION IN A CASSITERITE

In order to study this influence we carried out the four following experiments:

1. 0.5000 g of finely ground ore was fused with 4 g of Na_2O_2 in an iron crucible. After leaching the melt with 80 ml water in a 250 ml beaker, the solution was acidified by treating with 50 ml of HCl (d = 1.19). Then 1.5 g of iron powder was added to the solution, which was heated in a water-bath and filtered into a 500 ml conical flask. The filter was washed 6 times with 10% (v/v) HCl. A piece of aluminium wire 1.5 g was then introduced into the flask, which was stoppered as usual. After the Al was completely dissolved the flask was opened and 50 ml of HCl and 0.5 g of Al were added. After having stoppered the flask once more, the contents were boiled until all was dissolved, then cooled and titrated in the manner already described.
2. 0.5000 g of ore and 0.1508 g of MoO_3 (weight containing 0.1000 g Mo) were fused and treated in exactly the same way.
3. 0.5000 g of ore + 0.0754 g MoO_3 (equivalent to 0.0500 g Mo) were treated in the same way.
4. 0.0500 g of ore + 0.0151 g MoO_3 (equivalent to 0.0100 g Mo) were treated in the same manner.

All the experiments were duplicated. All the final solutions were greyish pink, which is perhaps due to the mixing of the orange colour of Mo(V) with the green colour of Fe(II).

The following results were obtained:

1. 41.10 ml
41.10 ml

2. 41.15 ml
41.20 ml

3. 41.10 ml
41.30 ml

4. 41.20 ml
41.20 ml

These figures help to confirm our previous conclusions that in solutions containing iron the interference of molybdenum is limited to a very slight increase in iodate consumption.

This very slight increase is within the limits of experimental errors, and therefore it seems worth while to make use of a modified method when tin concentrates containing Mo have to be analysed. Furthermore, Mo occurrence in tin concentrates is rare and never in large amounts.

But when the tin determination is carried out in some ores not yet worked, or in ore treatment residues, large amounts of Mo and small amounts of Sn may be found, and then a modified method must be used.

6. MODIFICATION OF TIN DETERMINATION METHOD IN ORES WHEN MOLYBDENUM IS PRESENT

The modification envisaged by us is based on the one already presented by LAMBIE AND SCHOELLER[10], in which Sn is retained by $Fe(OH)_3$ in strong ammonia medium, while Mo passes in solution.

As the molybdenum present in tin ores is generally in the form of MoS_2, the attack of the ore by HNO_3 would be enough to dissolve all the Mo. But in order to render soluble the wolfram that is almost always present in these ores, we tried the attack by strongly nitric aqua regia.

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Afterwards, without filtering, the solution is neutralized and made distinctly alkaline with ammonia in order to precipitate the iron present (if there is only a small amount of iron, as in cassiterites, we add an iron salt). The $Fe(OH)_3$ precipitate retains by adsorption the small quantity of tin that might have been dissolved by the action of aqua regia. After filtration we have in the precipitate all the tin, either as non-attacked cassiterite or as dissolved but retained by $Fe(OH)_3$. The wolfram and molybdenum (and copper if it exists) pass in the filtrate. The precipitate and paper are burned in an iron crucible, and the residue fused with Na_2O_2. After this point the tin determination is carried out as already described.

Procedure

(a) *In the absence of wolfram*

Place 0.5000 g of ore in a 250 ml beaker and add 50 ml HNO_3 (d = 1.50). Cover the beaker and then gently boil for two hours in order to effect the attack of the molybdenum ore. Cool and dilute to 120 ml. Now, if the iron content of the ore is very low, as in cassiterites, it is advisable to add some millilitres of an iron salt solution (say, 5 ml of a 10% $Fe_3(SO_4)_2$ solution). Neutralize, add an excess of 20 ml of NH_4OH (d = 0.925) and a small quantity of pulp. Boil for 2 minutes and filter immediately afterwards, washing with hot 2% solution of NH_4NO_3. If the Mo content of the ore is high it is advisable to dissolve the precipitate with diluted HNO_3 (1:1) and re-precipitate in the same way. If the Mo content is low it is not necessary to perform this operation.

Burn the precipitate and paper in an iron crucible, and proceed with the tin determination as already described.

(b) *In the presence of wolfram*

Place 0.5000 g of ore in a 250 ml beaker and add 50 ml HCl (d = 1.19). Cover the beaker and heat for 2 hours at 60-70° C. Remove the cover and, at the same temperature, evaporate to 10-15 ml. Add 10 ml conc. HNO_3 and evaporate again to 10 ml. Once more add 10 ml HNO_3 and evaporate. Dilute to 120 ml with water and follow, after this point, the method just described in (a).

This alteration of the attack is necessary because the wolframite is not easily attacked by HNO_3 alone.

Results

In order to verify the influences both of the attack and of the molybdenum in the final result, several experiments with a tin concentrate (Sn = 71.82%) were carried out. Table VI summarizes them.

TABLE VI

Experiment No.	*Ore taken g*	*MoO_3 taken g*	*HCl added ml*	*HNO_3 added ml*	*10% $Fe_2(SO_4)_3$ sol. added ml*	*Iodate consumed ml*
1	0.5000	—	directly fused with Na_2O_2		—	42.45
2	0.5000	—	directly fused with Na_2O_2		—	42.45
3	0.5000	—	—	70	5	42.40
4	0.5000	—	—	70	5	42.45
5	0.5000	—	50	10+10	5	42.35
6	0.5000	—	50	10+10	5	42.40
7	0.5000	0.1508	—	70	5	—
8	0.5000	0.1508	—	70	5	42.35
9	0.5000	0.1508	50	10+10	5	42.35
10	0.5000	0.1508	50	10+10	5	42.40

No marked difference among the figures obtained has been observed.

In order to verify the method with mixed ores of Sn-W-Mo, we have selected three samples with the following composition:

	Sample A	Sample B	Sample C
WO_3 %	20.57	18.34	25.00
Sn %	2.94	8.36	19.49

We carried out tin determinations in the samples, using the method described. In some experiments, a certain quantity of a molybdenum concentrate (molybdenite with 56.18% Mo) was added.

The results obtained are summarized in Table VII.

TABLE VII

Sample	*Weight taken* g	*Molybdenite added* g	*Iodate consumed* ml (1 ml = 0.00816 g Sn)	*Tin found* %	*Mean* %	*Differences* %
A	0.5000	—	1.80	2.94	2.97	+0.03
A	0.5000	—	1.85	3.01		
A	0.5000	0.5000	1.85	3.01		
A	0.5000	0.5000	1.80	2.94		
B	0.5000	—	5.10	8.32	8.32	−0.04
B	0.5000	—	5.15	8.40		
B	0.5000	0.5000	5.10	8.32		
B	0.5000	0.5000	5.05	8.24		
C	0.5000	—	11.95	19.50	19.52	+0.03
C	0.5000	—	12.05	19.66		
C	0.5000	0.5000	12.00	19.58		
C	0.5000	0.5000	11.85	19.32		

SUMMARY

The interference of molybdenum when tin is determined by iodate titration after reduction by aluminium, has been studied. A similar study was made of solutions also containing iron, and it was concluded that the interference in these solutions is almost non-existent. The results are discussed. A modified method for tin determination in ores containing molybdenum was proposed.

RÉSUMÉ

La perturbation causée par le molybdène lors du dosage de l'étain par titration au iodate, après réduction à l'aluminium, a été étudiée. Une étude analogue a été effectuée avec des solutions renferment également du fer; on est arrivé à la conclusion que l'interférence dans ces solutions est alors presque inexistante. Les résultats sont discutés. Une méthode modifiée pour le dosage de l'étain dans les minerais renfermant du molybdène a été proposée.

ZUSAMMENFASSUNG

Die durch Molybdän während der Bestimmung des Zinns mittels einer Titration mit Jodat nach Reduktion mit Aluminium, verursachte Störung wurde untersucht. Es wurde eine gleiche Untersuchung ausgeführt mit Lösungen, die ebenfalls Eisen enthalten. Man kam zu dem Schlusse, dass fast keine Störung in diesen Lösungen besteht. Die Resultate werden diskutiert. Es wird eine modifizierte Methode für die Bestimmung von Zinn in Mineralen, welche Molybdän enthalten, vorgeschlagen.

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TRICHLOROPHENOXYACETIC ACID AS A REAGENT FOR THE DETERMINATION OF THORIUM

by

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Phenoxyacetic acid was first used by PRATT AND JAMES[1] for the quantitative precipitation of thorium. But SMITH AND JAMES[2] showed later that the thorium salt of this acid was slightly soluble in water. RAO and co-workers[3] however, utilized this reagent for the estimation of thorium by the double precipitation method. DATTA AND BANERJEE[4] indicated its unsuitability for the determination of this metal and showed that substituted phenoxyacetic acids like guaiacoxy- and 2:4-dichlorophenoxyacetic acids were better reagents for thorium than the unsubstituted acid. This fact has further been confirmed in the present paper in which 2:4:5-trichlorophenoxyacetic acid (TCP or 2:4:5-T) has been successfully utilized for the gravimetric determination of thorium. Complete precipitation of thorium with this reagent takes place at a lower pH value *viz.* 2, the corresponding pH for 2:4-D is 2.8. Separation of thorium from metals such as Ca, Ba, Sr, Mg, Al, Ti, *etc.* and the rare earths can also be carried out by this reagent. Zirconium and iron (III) interfere and are co-precipitated along with thorium; iron however, could be separated by a very similar method[5] used in connection with 2:4-D.

EXPERIMENTAL

Reagents and chemicals

B.D.H. reagent grade 2:4:5-trichlorophenoxyacetic acid was purified by recrystallisation from hot water.

Stock solution of thorium, cerium, and lanthanum nitrates (Merck's reagent) were prepared and their earth contents were determined as usual. The solutions of other metals like Ca, Ba, Sr, Zr, Fe, and Ti *etc.*, were prepared from the AnalaR samples of nitrates and sulphates and the metals were estimated by the standard methods.

Analytical process

An aliquot quantity of thorium solution was diluted to 40 ml in a 250 ml beaker, neutralized to Congo-red and to it was added a hot 0.5% solution of 2:4:5-trichlorophenoxyacetic acid. A milky white precipitate appeared at once in the cold, which on continuous stirring or warming soon assumed a granular structure and collected at the bottom of the beaker. The solution should never be boiled as the precipitate becomes slimy and colloidal on boiling. The precipitate was filtered through Whatman No. 42 and washed with 0.1% reagent solution, followed by hot water. The paper and the contents were dried at 110 °C and charred and ignited to thorium oxide in a platinum crucible to a constant weight. The sodium salt of TCP was also used for this determination, to compare its effectiveness with that of the free acid. The procedure was the same, except that a cold solution of the sodium salt (1%) in water was employed. Some of the representative data are given in Table I.

TABLE I

ANALYSIS OF THORIUM SOLUTION USING TCP AND ITS NA-SALT

ThO_2 taken (oxalate method) g	*ThO_2 found by*			
	TCP g	*Diff.* mg	*Na-TCP* g	*Diff.* mg
0.0448	0.0446	−0.2	0.0448	±0
0.0380	0.0380	±0.0	0.0382	+0.2
0.0336	0.0334	−0.2	0.0335	−0.1
0.0224	0.0222	−0.2	0.0224	±0
0.0112	0.0111	−0.1	0.0113	+0.1
0.0056	0.0053	−0.3	0.0054	−0.2
0.0028	0.0025	−0.3	0.0025	−0.3
0.0014	0.0010	−0.4	0.0011	−0.3

Influence of pH on the precipitation of thorium

To find a suitable pH range for the complete precipitation of thorium, determinations were carried out with this reagent (free acid) at different acid concentrations. The pH of the solution was adjusted by adding ammonium acetate buffer. It appears from Table II, that complete precipitation commences from pH 2.

TABLE II

ESTIMATION OF THORIUM AT DIFFERENT pH VALUES

ThO_2 taken = 0.0336 g

pH	1.8	2	2.6	2.8	3.2	4	4.4	4.6
ThO_2 obtained (g)	0.0308	0.0332	0.0334	0.0336	0.0335	0.0334	0.0334	0.0332
Difference (mg)	−2.8	−0.4	−0.2	±0	−0.1	−0.2	−0.2	−0.4

Separation of thorium ion from the cerite earths

After preliminary experiments it was observed that extraction of thorium from a mixture of thorium-cerium and thorium-cerium-lanthanum could be carried out between pH 2 and 3.5, beyond which contamination of cerite earths occur with the thorium precipitate. The precipitate should be filtered by decantation and thoroughly washed on the filter several times with hot water. A set of results given in Table III, indicates that complete separation of thorium from solutions having thoria-earth oxide ratio up to 1:40, could be carried out with ease, and this ratio is also the same for 2:4-D. So in this respect, 2:4-D and TCP are found to be equally effective reagents for thorium.

Extraction of thorium from monazite sand

The sulphuric acid extract of monazite sand was prepared and purified according to the method of RAGHAVA RAO *et al.*[6]. The zirconium and phosphoric free extract was brought to pH 2.6 and thorium was precipitated from it by TCP according to the method described previously. Some of the representative data are given in Table IV.

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TABLE III

SEPARATION OF THORIUM FROM CERITE EARTHS

No.	ThO_2 taken g	CeO_2 added g	La_2O_3 added g	Approx. ratio of thoriacerite earths	ThO_2 obtained g
1.	0.0112	0.0120	—	1:1	0.0114
2.	0.0112	0.1200	—	1:10	0.0114
3.	0.0112	0.1200	0.1324	1:22	0.0115
4.	0.0112	0.1800	0.1324	1:28	0.0115
5.	0.0168	0.3600	0.1323	1:30	0.0172
6.	0.0168	0.3600	0.1986	1:33	0.0173
7.	0.0168	0.4800	0.1324	1:36	0.0173
8.	0.0168	0.4800	0.1986	1:40	0.0174
9.	0.0112	0.3600	0.1324	1:46	0.0124

TABLE IV

Weight of the sample	TCP		m-Nitrobenzoic acid	
	ThO_2 obt.	% recovery of ThO_2	ThO_2 obt.	% recovery of ThO_2
g	g		g	
1.255	0.0916	7·31	0.0918	7·32
1.255	0.0918	7·32	0.0916	7·31
1.232	0.0901	7·31	0.0903	7·32
1.232	0.0899	7·30	0.0901	7·31
1.232	0.0902	7·32	0	—

Separation of thorium from other elements

TCP can separate thorium from a number of common elements such as, Ca, Ba, Sr, Al, Zn, Mg and Ti within a pH range from 2 to 4. Unlike 2:4-D double precipitation is not necessary with this reagent for the removal of Co, Ni or Cr (see Table V). Zr and Fe (III) are coprecipitated with Th. Uranium also interferes when present in large amounts; considerable quantities, however, can be removed by double precipitation. The results of such separation have been given in Table VI, and they indicate that thorium can be separated by this reagent from solutions having ThO_2-U_3O_8 ratio up to 1:25 by the double precipitation method[7]. Each figure represents the mean of three estimations.

TABLE V

SEPARATION OF THORIUM FROM FOREIGN IONS

ThO_2 taken mg	Metal oxide added	Amount in mg	ThO_2 obt. mg
22.0	CaO	19.10	22.0
22.0	BaO	22.1	22.1
22.0	SrO	31.5	22.2
22.0	MgO	23.8	22.4
22.0	ZnO	19.8	22.4
22.0	NiO	20.3	22.5
22.0	CoO	19.6	22.4
22.0	Cr_2O_3	21.5	22.6
22.0	TiO_2	27.5	22.4

TABLE VI

SEPARATION OF THORIUM FROM URANIUM

No.	*ThO_2 used*	*U_3O_8 added*	*Th : U oxide ratio (approx.)*	*ThO_2 found*	
				single pptn.	*double pptn.*
	g	*g*		*g*	*g*
1.	0.0168	0.0225	1:1.3	0.0170	—
2.	0.0168	0.0341	1:2	0.0171	—
3.	0.0168	0.0566	1:3.3	0.0172	—
4.	0.0112	0.0566	1:5	—	0.0114
5.	0.0112	0.1132	1:10	—	0.0115
6.	0.0112	0.1698	1:15	—	0.0116
7.	0.0112	0.2264	1:20	—	0.0118
8.	0.0112	0.2830	1:25	—	0.0119

Separation of iron (III) from thorium and their co-determination

Iron and thorium are both precipitated by TCP. It is not possible to separate them by adjusting the acid concentration of the mixture. They may however be separated with the help of ammonium carbonate as in the case with 2:4-D[5]. The pH of the mixture containing thorium and iron was brought to 2.6, as at this pH both the iron and thorium are completely precipitated. To this solution in the cold, was added a hot 0.5% solution of TCP, till the precipitation was complete. The solution should not be boiled, as then the iron salt turns somewhat oily and sticks to the sides of the beaker. The mixed precipitate was filtered and washed with 50 % alcohol.

TABLE VII

SEPARATION OF IRON FROM THORIUM

ThO_2	*Fe_2O_3*	*$(NH_4)_2CO_3$ (5%)*	*Ratio of ThO_2-Fe_2O_3 (approx.)*	*Oxides obtained*	
				ThO_2	*Fe_2O_3*
g	*g*	*ml*		*g*	*g*
0.0112	0.0051	5	2:1	0.0093	0.0068
0.0112	0.0102	5	1:1	0.0089	0.0070
0.0112	0.0102	10	1:1	0.0108	0.0103
0.0112	0.0102	12	1:1	0.0109	0.0103
0.0112	0.0102	15	1:1	0.0109	0.0105
0.0112	0.0102	20	1:1	0.0116	0.0101
0.0224	0.0204	30	1:1	0.0216	0.0205
0.0112	0.0204	15	1:2	0.0101	0.0213
0.0112	0.0306	20	1:3	0.0098	0.0314

The precipitate was transferred to a beaker and to it was added with constant stirring a 5% solution of ammonium carbonate, avoiding excess (10-15 ml of 5% ammonium carbonate was just enough to dissolve a ppt. having about 11 mg of ThO_2) to dissolve the thorium salt completely. The residual precipitate of iron was filtered by decantation, washed with a little 1% solution of ammonium carbonate solution and finally with warm water. The precipitate was then dissolved in dil. HCl, the pH was adjusted to 2.6 and iron was reprecipitated with 5% ammonium carbonate, to free it from any Th, a small quantity of which was always retained by the iron precipitate.

The filtration and washing were done as before. Iron was estimated gravimetrically. The combined filtrates were boiled with a little conc. hydrochloric acid so as to decompose the thorium-ammonium carbonate - complex, the pH was adjusted to the desired value and thorium was re-precipitated with the reagent solution as before. From the results, indicated in Table VII, it is seen that the method works fairly well in a mixture having thoria-iron oxide ratio up to 1:1.

Composition of thorium salt of TCP and possibility of direct weighing

To test the possibility of adopting the direct weighing method for the determination of thorium with this reagent, the procedure previously described was followed, except that a weighed sintered glass crucible replaced the filter paper and filtration and washings were carried out with the aid of suction. After washing free of excess of TCP by boiling water followed by hot alcohol, the precipitate was dried at 110° C and weighed. Aliquot quantities of the dried salt were ignited to the oxide. The results indicated that the salt contained three acid residues attached to one thorium containing one (OH) group, in the molecule, associated with one molecule of water; the composition is therefore very similar to that of the thorium salt of 2:4-D. The salt was analysed for its chlorine content by Piria and Schiff's method; the value obtained also supports the formula.

Recovery of the reagent

Though the thorium salt of TCP is basic in type, it may be determined satisfactorily by a direct weighing method (Table VIII). From this thorium salt the reagent may be recovered to a considerable extent and this is a great advantage as TCP is a very costly reagent. The thorium salt was dissolved in the least quantity of ammonium carbonate (dil.), then acidified with conc. hydrochloric acid and boiled. On cooling, fine crystals of TCP deposited. The crystals were filtered, washed several times with cold water, till free from chlorides and then they were dried at 105° C and weighed. The results in Table IX show that as much as 65% of TCP could be recovered in this way.

TABLE VIII

ESTIMATION OF Th BY DIRECT WEIGHING METHOD

No.	*Th-salt dried at 110°* g	*ThO_2 found on ignition* g	*ThO_2 calc. from salt* g	*Cl_2 in dry salt* found g	calc. g
1.	0.0451	0.0224	0.0215	0.0102	0.0099
2.	0.0226	0.0114	0.0108	0.0054	0.0049
3.	0.0705	0.0330	0.0336	0.0160	0.0154
4.	0.0348	0.0158	0.0166	0.0070	0.0077
5.	0.0780	0.381	0.0372	0.0168	0.0171

TABLE IX

RECOVERY OF TCP FROM ITS Th-SALT

No.	*Th-salt taken (110°)* g	*TCP obt.* g	*% recovery*
1.	0.4865	0.1682	65.3
2.	0.2440	0.0802	62.2
3.	0.3642	0.1279	66.4
4.	0.1831	0.0649	66.8

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SUMMARY

2:4:5-trichlorophenoxyacetic acid has been successfully used for the determination of thorium. It has been proved to be a better reagent for thorium than 2:4-dichlorophenoxyacetic acid as it produces quantitative precipitation of thorium at a considerably lower pH value and can separate Th from a number of common elements, such as Ca, Ba, Sr, Zn, Co, Ni, Ti, U, *etc.* and cerite earths more effectively. Zr and Fe interfere, but iron may be removed by a convenient method. Direct weighing may be applicable for the estimation of thorium within the limits of experimental error.

RÉSUMÉ

L'acide 2,4,5-trichlorophénoxyacétique a été utilisé avec succès pour le dosage du thorium. Il constitue un meilleur réactif pour le thorium que l'acide 2,4-dichlorophénoxyacétique; il précipite quantitativement le thorium à des pH beaucoup plus bas et permet de séparer ce cation d'un certain nombre d'éléments courants tels que Ca, Ba, Sr, Zn, Co, Ni, Ti, U, *etc.* et les terres cériques. Zr et Fe gênent, mais le fer peut être éliminé préalablement. La pesée directe peut être effectuée pour le dosage du thorium, dans les limites de l'erreur expérimentale.

ZUSAMMENFASSUNG

Die 2,4,5-Trichlorophenoxyessigsäure wurde mit Erfolg für die Bestimmung von Thorium angewendet. Sie ist ein besseres Reagenz für Thorium, als die 2,4-Dichlorophenoxyessigsäure. Sie fällt das Thorium quantitativ bei viel niedrigeren pH-Werten und erlaubt dieses Kation von einer gewissen Anzahl von gebräuchlichen Elementen wie Ca, Ba, Sr, Zn, Co, Ni, Ti, U, *etc.* und den Cersalzen abzutrennen. Zr und Fe stören, aber das Eisen kann vorher eliminiert werden. Man kann für die Bestimmung von Thorium direkt in den experimentellen Fehlergrenzen wägen.

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THE DIRECT WEIGHING OF ZIRCONIUM TETRAMANDELATE

by

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In the determination of zirconium by precipitating with mandelic acid, the zirconium tetramandelate precipitate is usually ignited to the oxide for weighing. ASTANINA AND OSTROUMOV[1] reported that zirconium tetramandelate may be weighed directly after being washed with 95% ethyl alcohol.

A more comprehensive study was made by BELCHER, SYKES, AND TATLOW[2]. These investigators recommended that the precipitate of zirconium tetramandelate be washed with a saturated aqueous solution of zirconium tetramandelate. Slightly low results were obtained but this was compensated by multiplying the observed weight by a factor, 1.0145. Attempts to explain the low results by the partial decomposition of the mandelic acid to form phenyl glyoxylic acid were unsatisfactory. The authors conclude "The reasons for the non-stoichiometry of the complexes of zirconium and mandelic acid are still unknown . . . . . ."

We believe that the non-stoichiometry of the zirconium tetramandelate precipitate can be explained by the precipitation of varying amounts of basic salts such as $ZrO(C_8H_7O_3)_2$ and $Zr(OH)(C_8H_7O_3)_3$ along with the pure zirconium tetramandelate, $Zr(C_8H_7O_3)_4$. If this hypothesis were true, best results should be obtained in strongly acid solutions where hydrolysis of the zirconium ion is at a minimum. In order to test this hypothesis the following experiment was devised:

Solutions of zirconyl chloride containing a fixed amount of zirconium oxide (25.30 mg) were treated with varying amounts of hydrochloric acid. The volume was brought up to 50 ml by the addition of distilled water. 25 ml of 1*M* mandelic acid (15%) was added and the samples heated to 85°-90° C for about 45 minutes. The solutions were set aside to cool, then filtered through sintered glass crucibles. The precipitates were washed with a saturated solution of zirconium tetramandelate[2] followed by three 10 ml portions of 95% ethanol and finally with two 10 ml portions of ethyl ether. The precipitates were dried at 110° C to constant weight (about 1 hour), then weighed. The results are given in Table I.

These data indicate that the concentration of hydrochloric acid present at the time of precipitation has a great influence upon the composition of the zirconium mandelate precipitate. Those precipitates formed in weakly acid solution probably correspond to a basic salt of composition, $ZrO(C_8H_7O_3)_2$. As the acidity is increased the composition approaches that of $Zr(OH)(C_8H_7O_3)_3$ while only in very strongly acidic

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TABLE I

EFFECT OF HYDROCHLORIC ACID CONCENTRATION ON WEIGHT OF ZIRCONIUM MANDELATE PRECIPITATES (25.30 mg ZrO_2 USED IN ALL EXPERIMENTS)

Concentration of hydrochloric acid in final solution	*Wt. of zirconium mandelate precipitate g**	*Wt. ZrO_2 calculated mg*
0	0.0732	12.96
0	0.0671	11.88
0	0.0698	12.36
0	0.0699	12.38
0.3*M*	0.1041	18.44
	0.0995	17.62
	0.1035	18.33
	0.1040	18.42
0.8*M*	0.1243	22.01
	0.1239	21.94
	0.1239	21.94
	0.1241	22.00
1.5*M*	0.1305	23.11
	0.1308	23.16
3.0*M*	0.1384	24.51
	0.1383	24.49
4.5*M*	0.1398	24.76
	0.1411	25.00
	0.1426**	25.25
	0.1429**	25.31
7.5*M*	0.1423	25.20
	0.1426	25.25
	0.1422**	25.18
	0.1425**	25.24

* $Zr(OH)_3(C_8H_7O_3)$ would give 0.0602 g
$ZrO(C_8H_7O_3)_2$ would give 0.0840 g
$Zr(OH)(C_8H_7O_3)_3$ would give 0.1152 g
$Zr(C_8H_7O_3)_4$ would give 0.1429 g
** Mandelic acid solution added dropwise over a period of 30 minutes.

solution is the normal zirconium tetramandelate obtained. It is of interest to note that quantitative precipitation of the zirconium occurs at all acidities. Identical amounts of zirconium oxide are obtained upon ignition of any of these precipitates[3].

In calculating the weights of zirconium oxide the theoretical factor,

$$\frac{ZrO_2}{Zr(C_8H_7O_3)_4} = 0.1771$$

was used. No correction factor was applied. It was found that a coarser, more crystalline precipitate was obtained when the mandelic acid was added dropwise, with constant stirring, to a hot solution containing zirconium. The time required for drying the precipitate was shortened considerably by washing the precipitate with 95% ethanol and finally with ethyl ether. These organic solvents would be effective also in dissolving any free mandelic acid carried down in the precipitate.

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If a precipitate of zirconium tetramandelate is to be used for direct weighing the following precautions are recommended:

(1) The solution be strongly acid with hydrochloric acid; 5*M* or more.

(2) The mandelic acid be added dropwise with constant stirring to the hot (85°-90° C) acid solution.

(3) The solution be allowed to cool before filtration.

(4) The precipitate be washed with a saturated solution of zirconium tetramandelate followed by 95% ethyl alcohol and finally with ethyl ether.

SUMMARY

The non-stoichiometry of zirconium tetramandelate precipitates is explained by the presence of basic salts of varying composition. For reproducible results the zirconium tetramandelate should be precipitated from hot, strongly acid solution by the dropwise addition of mandelic acid.

RÉSUMÉ

Le fait que le mandélate de zirconium ne précipite pas dans des proportions stoechiométriques, est expliqué par la formation de sels basiques de composition variable. Pour obtenir des résultats reproductibles, il est nécessaire de précipiter le zirconium en solution très chaude et fortement acide, en ajoutant l'acide mandélique goutte à goutte.

ZUSAMMENFASSUNG

Das nicht stöchiometrische Verhalten von Fällungen von mandelsaurem Zirkonium wird mit der Anwesenheit basischer Salze von veränderlicher Zusammensetzung erklärt. Um reproduzierbare Resultate zu erhalten, muss man mandelsaures Zirkonium aus heisser, stark saurer Lösung unter tropfenweiser Zugabe von Mandelsäure ausfällen.

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MICRO-GRAVIMETRIC DETERMINATION OF LEAD WITH THIONALIDE

by

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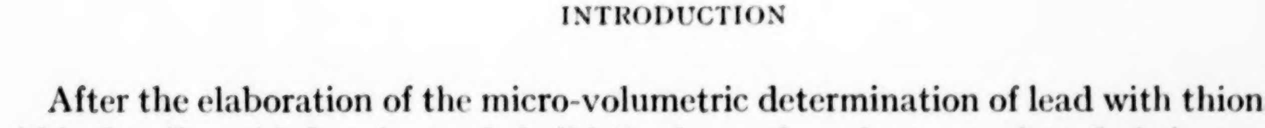
INTRODUCTION

After the elaboration of the micro-volumetric determination of lead with thionalide (thioglycolic acid β-aminonaphthalide)[1], the authors have continued their research in order to evolve a micro-gravimetric determination of lead with the same reagent. The macro method has been proposed by BERG[2].

To that end, the various factors affecting this determination, such as: (1) the amount of lead, (2) the reagents used to establish the weakly alkaline medium prior to the precipitation, (3) the amount of reagent and the method of its introduction, (4) the wash liquids used, (5) the temperature and the time required to dry the precipitate, were studied. Based on these investigations, an exact micro-gravimetric method has been evolved, applying EMICH'S[3] micro-technique and using a porcelain filterstick.

Principle of the method[6]

Lead cation is precipitated from a weak sodium hydroxide solution, containing potassium cyanide and sodium potassium tartrate, with an acetone solution of thionalide:



The filtered and washed precipitate is dried at 110° C[4]. Lead is calculated from the weight of the precipitate obtained.

EXPERIMENTAL

Reagents and solutions employed were:

1. Lead nitrate solution (prepared by dissolving 2 g of pure lead metal in conc. nitric acid, evaporating excess acid and making up to 1 litre with bi-distilled water. The solution, therefore, contained 2 mg of lead per ml).
2. 1% Phenolphthalein (alcoholic solution).
3. Sodium carbonate solution 2*N*.
4. Ammonium hydroxide, conc.

5. Sodium hydroxide solution $2N$.
6. Potassium cyanide.
7. Sodium potassium tartrate.
8. Thionalide.
9. Acetone.
10. Acetone-water (mixture 1 : 1).
11. Sulphuric acid (1 : 5).
12. Iodine solution $0.1N$.
13. Bi-distilled water was used throughout.

Procedure recommended for the micro-gravimetric determination of lead

The slightly acid solution of lead cation (2-5 mg lead in 1-3 ml) is introduced into a previously dried and weighed Pyrex glass micro-beaker (dimensions of the beaker: height 55 mm, outer diameter 18 mm), the volume is made up to 3 ml with bi-distilled water, about 50 mg of sodium potassium tartrate is added and the solution is stirred with a short, bent stirring rod[*] to dissolve the tartrate. 1 drop of phenolphtalein solution is introduced and $2N$ sodium hydroxide solution is added dropwise, until the precipitate of lead hydroxide, which forms at first, is just redissolved and the solution tinted red[**]. 100 mg approx. of potassium cyanide are now added and the solution is heated to 80° C (temperature of the solution) on a micro drying block[6]. A freshly prepared solution of 30-40[***] mg of thionalide in 1-2 ml of acetone is introduced in small drops from a pipette; throughout the addition of the reagent, the solution is stirred vigorously with the stirring rod, particular care being taken that no drop of reagent falls on the sides of the beaker or on the stirring rod. The mixture is cautiously heated for 1-2 minutes at about 80° C on the drying block, the precipitate allowed to settle for another 1-2 minutes, and filtered, while the solution is still hot and using low suction, through a porcelain filterstick[****].

The beaker, stirring rod, filterstick and precipitate are washed with:

a. Acetone-water (mixture 1 : 1):
    2×3 ml
    $3 \times 1\frac{1}{2}$ ml
b. Water:
    3×2 ml
c. Acetone-water (mixture 1 : 1):
    1×1 ml

In this way the precipitate is freed from both excess thionalide and inorganic ions present during precipitation.

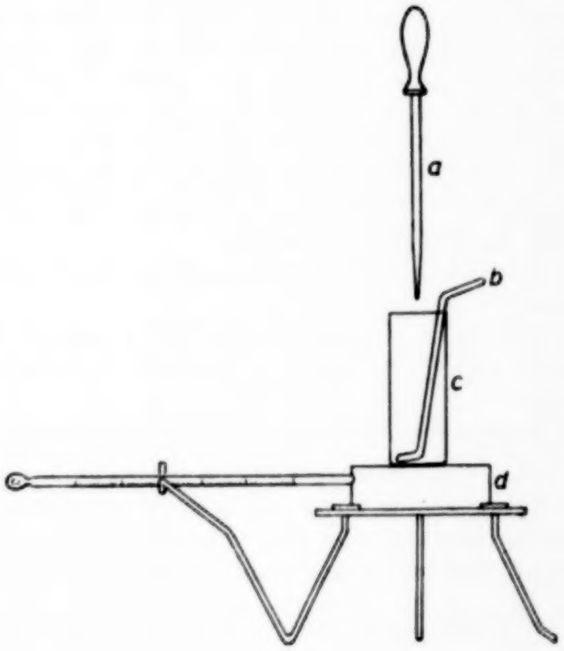


Fig. 1. Apparatus used for precipitation.
a. dropping pipette
b. bent glass stirring rod
c. micro-beaker
d. micro drying block with thermometer

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[*] The stirring rod is shaped as shown in Fig. 1. The upper handle serves for stirring, while the lower bent part facilitates scraping off the precipitate whenever this has been sucked too close to the filterplate, impeding filtration and washing. This is done easily with this rod, without taking the filterstick out of the micro-beaker. No loss of precipitate can, therefore, occur in this operation.

[**] If the solution is strongly alkaline, the lead thionalide precipitate either does not form at all, or does not form quantitatively[5].

[***] 30 mg of thionalide for 2-3 mg of lead;
40 mg of thionalide for 4-5 mg of lead.

[****] The dimensions of the filterstick used were: overall diameter 11 mm; stem diameter 3-4 mm; overall height 55 mm. All filtersticks used were U.S.A. Produce, made by Coors Porcelain Co., Golden.

The last portion of wash liquid (c) is collected into a small test tube and examined, on a spot plate, for the presence of thionalide, as follows: 0.5 ml of the wash liquid (acetone-water mixture 1 : 1) is introduced into a depression of a black, glazed porcelain spot plate, 1 drop of sulphuric acid (1 : 5) and 1 drop of 0.1N iodine solution are added and the mixture stirred vigorously with a glass rod. In the presence of at least 10 micrograms (γ) of thionalide, a white, floccular precipitate of dithionalide is formed within 2 minutes; the precipitate is best observed in daylight:

$$2C_{10}H_7NHCOCH_2SH + I_2 \longrightarrow C_{10}H_7NHCOCH_2\text{-}S\text{-}S\text{-}CH_2CONHC_{10}H_7 + 2HI$$

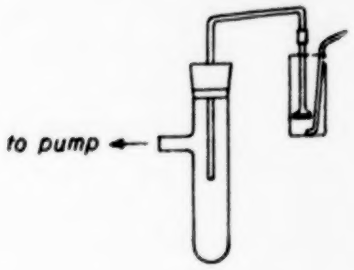

Fig. 2. Apparatus for filtration.

Remark: the same test may be applied to the micro-volumetric determination of lead with thionalide[1].

If no thionalide is detected, the filterstick is detached from the suction system and the microbeaker, containing the precipitate, together with the filterstick and the stirring rod are dried in a drying block of BENEDETTI-PICHLER[7] at 110° C[4] (temperature inside the drying tube; to that end the temperature of the drying block must be 120 °C), using low suction, for 15 minutes; after that period, the drying tube containing the beaker, the filterstick and the stirring rod is taken out of the drying block and cooled outside the block for 15 minutes, without interrupting the suction. After cooling, the beaker together with the filterstick and the stirring rod are removed from the tube, the beaker and the handle of the stirring rod wiped, as usual, first with a damp flannel cloth and next with two sets of chamois skins, left for 15 minutes on a nickel block near the micro-balance, 5 minutes on a nickel block inside the balance, and finally 5 minutes on the pan of the balance. The beaker, together with the filterstick and the stirring rod, is weighed in the twenty-fifth minute.

The weight of the precipitate, multiplied by the factor 0.3239, gives the amount of lead in the sample.

The time required for 1 determination is 2½ hours approx. (including preparation of the beaker and the filterstick); 2 parallel determinations may be carried out in about 4 hours.

Cleaning the filterstick, stirring rod and beaker after the determination

Cleaning the utensils is effected by washing them alternately with HNO_3-H_2O (1 : 1) and acetone a few times, and then 2-3 times with bi-distilled water, using portions of approx. 5 ml each time. Drying and weighing of the utensils is carried out as described above under the procedure recommended for the micro-gravimetric determination of lead.

Table I shows some characteristic results obtained by the above method.

Conclusion

As indicated by Table I, results are exact (maximum relative error ± 0.4% for 2-5 mg of lead; for 1 mg of lead, maximum relative error was ± 0.6%; exp. No. 1-20 and 21-25 respectively).

General discussion of the factors affecting the determination of lead by the proposed method

1. The method was established with samples containing 3 mg of lead (this amount of lead was chosen, as it had proved most convenient during the micro-volumetric experiments[1]); it was next tested successfully on samples containing 2-5 mg of lead, samples containing 1 mg could still be determined, but the maximum relative error reached ± 0.6%; samples over 5 mg gave a precipitate of lead thionalide which was too bulky to be handled comfortably under the experimental conditions established. Consequently, 2-5 mg of lead were chosen as suitable limits for this determination.
2. In the micro-volumetric method[1], neutralization of the sample solution was effected by the addition of conc. ammonium hydroxide up to the neutralization of

the solution as indicated with phenolphtalein, and an equal volume of 2*N* sodium carbonate solution was then added. In the course of their subsequent experiments, the authors have found it advantageous to replace these reagents with 2*N* sodium hydroxide solution, added dropwise until the precipitate of lead hydroxide, formed at first, is redissolved and the solution tinted red[5]. The sample solution treated this way may be heated without danger of the appearance of the white turbidity, which sometimes made it necessary to discard samples neutralized by the former method. The use of sodium hydroxide solution, instead of the conc. ammonium hydroxide and the 2*N* sodium carbonate solution, can therefore be also recommended for the micro-volumetric method[1].

TABLE I

MICRO-GRAVIMETRIC DETERMINATION OF LEAD WITH THIONALIDE

Exp. No.	*Excess of thionalide* %	*Pb present* *mg*	*Pb found* *mg*	*Pb difference* *mg*	*Relative error* %
1	200	2.000	1.993	−0.007	−0.3
2	200	3.000	3.009	+0.009	+0.3
3	200	4.000	4.010	+0.010	+0.25
4	200	5.000	4.987	−0.013	−0.3
5	300	2.000	2.008	+0.008	+0.4
6	300	3.000	2.990	−0.010	−0.3
7	300	4.000	4.013	+0.013	+0.3
8	300	5.000	5.005	+0.005	+0.1
9	400	2.000	2.005	+0.005	+0.25
10	400	3.000	2.994	−0.006	−0.2
11	400	4.000	3.987	−0.013	−0.3
12	400	5.000	5.010	+0.010	+0.2
13	500	2.000	2.008	+0.008	+0.4
14	500	3.000	3.010	+0.010	+0.3
15	500	4.000	4.014	+0.014	+0.35
16	500	5.000	5.012	+0.012	+0.25
17	600	2.000	2.007	+0.007	+0.35
18	600	3.000	3.010	+0.010	+0.3
19	600	4.000	3.988	−0.012	−0.3
20	600	5.000	5.016	+0.016	+0.3
21	200	1.000	1.006	+0.006	+0.6
22	300	1.000	0.995	−0.005	−0.5
23	400	1.000	1.005	+0.005	+0.5
24	500	1.000	1.006	+0.006	+0.6
25	600	1.000	0.994	−0.006	−0.6

3. Experience soon showed that the method of introducing the reagent into the sample was a salient factor, affecting the results more than any other of the factors investigated. It was found of definite advantage to add the thionalide solution to the previously heated sample solution; where this was not done, excess thionalide occasionally precipitated in a form which could not be completely removed by subsequent heating and washing, thus causing high results.* This was demonstrated by carrying out blank experiments, *i.e.* following the usual procedure, but with

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* The tall and narrow shape of the micro-beaker, used in the micro-gravimetric method, makes effective washing and removal of excess thionalide difficult; it was considered better to prevent, as far as possible, any excess thionalide from settling out of the solution, rather than remove it by washing after it had settled out. This could be done by heating the solution previous to the addition of thionalide and filtering while the solution is still hot.

bi-distilled water substituted for the lead nitrate solution. The thionalide not removed by washing could be observed on the sides of the beaker. Where these utensils were dried and weighed according to the procedure recommended, the amount of thionalide not removed was appreciable.

As a result of these investigations, the addition of thionalide was henceforth carried out after the sample solution had been heated to about 80° C; the thionalide was added in small drops from a pipette, with continuous and vigorous stirring. Care was taken not to let any drops fall on the stirring rod or the sides of the beaker, as the thionalide settling out on those was found difficult to remove quantitatively.

Experiments proved that the procedure recommended gave exact results whenever a 200%-600% excess of reagent was used, *i.e.* approx. 6-14 mg thionalide for each mg of lead present (see Table I). In practice it was found convenient to use 30 mg of thionalide for 2-3 mg of lead and 40 mg of thionalide for 4-5 mg of lead.

4. The washing recommended in the a.m. procedure was found adequate in the experiments carried out; in order, however, to prevent any unsuccessful determination due to incomplete washing, the last portion of the wash liquid was tested for the presence of thionalide, as indicated in the procedure recommended for the microgravimetric determination of lead with thionalide.

5. The temperature chosen for drying the precipitate lies within the plateau of DUVAL's thermogravimetric curve[4] for lead thionalide. The drying time of 15 minutes has been proved adequate by numerous experiments.

SUMMARY

The authors have elaborated an exact micro-gravimetric method for the determination of lead with thionalide.

RÉSUMÉ

Les auteurs ont élaboré une micro-méthode gravimétrique exacte pour la détermination du plomb au moyen de thionalide.

ZUSAMMENFASSUNG

Die Verfasser haben eine exakte mikro-gravimetrische Methode zur Bestimmung des Bleis mit Thionalid ausgearbeitet.

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RECHERCHES SUR LE DOSAGE DE LA CELLULOSE

par

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La méthode la plus universellement utilisée pour le dosage de la cellulose est celle de la station agronomique de Weende[1] mais les modes opératoires qui en dérivent sont très variables et donnent lieu à des divergences de résultats.

D'autres méthodes ont été proposées par KURSCHNER[2], BERTRAND[3], CROSS ET BEVAN[4], ALQUIER[5], GUILLEMET[6], *etc.* Une étude de certaines de ces techniques a été faite au Laboratoire de Zootechnie de l'Institut Agronomique[7] montrant les résultats différents que l'on obtient avec ces diverses méthodes qui ne déterminent pas le ou les mêmes produits. Ainsi la méthode de Weende donnerait un mélange de cellulose vraie, de lignine et d'une fraction des polyholosides non cellulosiques.

Le calcul de la valeur fourragère d'un aliment dépend pour une part importante de son taux de cellulose, les tables de Kellner donnant, d'une part, le coefficient de digestibilité de la matière protéique et de la matière organique en fonction du taux de cellulose par rapport à la matière sèche et, d'autre part, le coefficient à utiliser pour la transformation de la matière organique digestible, en unités fourragères. Et malgré ses imperfections, la méthode de Weende a été adoptée en France par les Industries de l'Alimentation animale[8], aux Etats Unis par l'Association of Official Agricultural Chemists[9] et en Belgique par les Laboratoires du Ministère de l'Agriculture[10], car elle donne des résultats reproductibles lorsqu'elle est utilisée exactement dans les mêmes conditions ainsi qu'une expérience de plus de 15.000 dosages de cellulose effectués dans notre Laboratoire de Contrôle nous permet de l'affirmer.

Cependant, nous avons examiné dans notre Laboratoire de Recherches, les différentes méthodes données sous le nom de méthode de Weende qui diffèrent les unes des autres par certains détails ainsi qu'on peut le constater dans les publications ci-dessus mentionnées[8,9,10].

Ainsi, nous avons pu constater que la filtration sur creuset d'alundum adoptée par les Industries de l'Alimentation animale était bien préférable à toute autre filtration: Büchner, toiles de bronze, creuset de Gooch.

Nous avons pu aussi déterminer qu'il était indispensable de définir parfaitement les conditions de la calcination finale et que les meilleures conditions étaient une calcination de 2 heures exactement à 700° C dans un four électrique à régulation automatique de température, l'instant 0 étant celui où la température atteint 700°.

Mais nos efforts ont porté particulièrement sur les lavages dont dépendent pour une part les résultats donnés par la méthode. Après la première attaque acide, le

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résidu doit être lavé jusqu'à cessation de réaction acide et après l'attaque alcaline le résidu doit être lavé jusqu'à cessation de réaction alcaline. Nous avons pensé que l'on pourrait remplacer ces lavages par des neutralisations et nos essais ont donné entière satisfaction ainsi que les quelques chiffres ci-après le montrent (taux de cellulose exprimée en g pour 100 g).

	Méthode par lavages	Méthode par neutralisations
Coton hydrophile	88.3	88.5
Luzerne	31.5	31.5
Pâtes alimentaires	1.7	1.7
Farine de blé	2.5	2.5
Levure de distillerie	6.7	6.5
Graines fourragères diverses	1.7	1.8
Pâtes alimentaires	0.6	0.6
Luzerne	27.0	27.1
Tourteau de tournesol	18.3	18.5
Tourteau d'arachide	14.5	14.3
Farine de blé	2.5	2.5
Luzerne	28.9	29.2
Aliment vaches laitières	10.0	9.7
,, poussins	5.7	5.8
,, vaches laitières	12.4	12.6
,, porcelets	4.8	4.9
,, vaches laitières	8.6	8.6
,, porcs	8.0	8.0
,, chiens	3.0	3.0
,, poules	5.5	5.5
,, veaux	3.7	3.7
,, vaches laitières	9.6	9.8
,, poules pondeuses	6.1	6.3
,, porcs	9.1	9.1

Les deux méthodes donnent donc les mêmes chiffres, la méthode par neutralisation ayant tendance toutefois à donner des résultats très légèrement plus forts. Mais ces résultats sont plus normaux car ainsi les attaques acide et alcaline sont nettement délimitées. Nous avons eu d'ailleurs des litiges avec un laboratoire qui donnait systématiquement des taux inférieurs aux nôtres; après enquête, la cause de cette diminution due au fait que la personne chargée de ces dosages arrêtait les attaques alcalines au moment d'aller déjeuner et effectuait les lavages deux heures plus tard, de sorte que le liquide se refroidissait lentement en restant basique, l'attaque se continuait donc, d'où une erreur par défaut. Avec la méthode par neutralisations il n'y a rien à craindre de ce genre du moment qu'on laisse les solutions d'attaque après le stade de la neutralisation. Nous avons d'ailleurs constaté l'influence des lavages par des eaux alcalines ou par des eaux acides, d'où l'intérêt encore accru de la méthode par neutralisations, car un liquide contenant de la cellulose en suspension

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ne doit être laissé ni en milieu fortement acide ou alcalin ni en milieu faiblement acide ou alcalin. Or, il faut plusieurs lavages pour arriver à réaction non acide ou non alcaline et pendant toute la durée de ces lavages l'attaque du résidu se produit lentement mais notablement.

Nous avons enfin étudié deux méthodes:

1° celle de l'Ecole d'Agronomie de Gembloux (Belgique) qui comporte une seule attaque par un mélange de 80 ml d'acide acétique, 10 ml d'acide nitrique et d'eau q s p 100; elle donne par rapport à la méthode de Weende les résultats ci-après:

	Méthode de Weende modifiée	Méthode Gembloux
Pâtes alimentaires	0.5	1.1
Luzerne	23.0	18.3

2° celle de la faculté de Pharmacie de Madrid[11] qui comporte une seule attaque par un mélange de 2 g d'acide trichloracétique, 5 ml d'acide nitrique et 75 ml d'acide acétique au 1/3; elle donne par rapport à la méthode de Weende les résultats ci-après:

	Méthode de Weende modifiée	Méthode de la Faculté de Pharmacie de Madrid
Aliment Poussins	3.8	4.9
Luzerne	28.8	23.4

Ces deux méthodes donnent donc des résultats trop élevés pour les produits à faible teneur en cellulose et des résultats trop faibles pour les produits à fortes teneurs en cellulose. De plus, la méthode espagnole ne tient pas compte des matières minérales restant avec la cellulose en fin de dosage, ce qui constitue une erreur, car tous les produits végétaux contiennent une certaine quantité de matières minérales dont une partie reste insoluble après attaque et ne doit donc pas être comptée en cellulose.

Mode opératoire

La méthode de Weende modifiée telle que nous l'utilisons est la suivante:

Peser 1 g d'échantillon que l'on introduit dans le ballon de l'appareil à reflux avec 100 ml d'acide sulfurique titré à 1.25%; porter à douce ébullition pendant 30 minutes exactement (instant 0 compté au commencement de l'ébullition); agiter toutes les cinq minutes; dès la fin de cette attaque, transvaser dans un godet en verre de centrifugeur et centrifuger 4 minutes (force centrifuge 4450 g); aspirer la plus grande partie du liquide surnageant, ajouter 5 gouttes de bleu de bromothymol à 1%, neutraliser à la goutte avec la soude 2.5%, réajouter le liquide restant dans le ballon, rincer et terminer la neutralisation en ajustant à pH 7 avec l'aide supplémentaire de papier indicateur; centrifuger 4 minutes et aspirer le liquide surnageant en laissant 20 ml de liquide au fond du godet.

Transvaser quantitativement ce résidu dans le ballon utilisé dans l'opération précédente, rincer avec 30 ml d'eau et ajouter 50 ml de soude 2.5%; porter à une douce ébullition exactement 30 minutes; dès la fin de cette attaque, transvaser dans un godet de centrifugeur et centrifuger 4 minutes;

aspirer la plus grande partie du liquide surnageant et neutraliser avec l'acide sulfurique 1.25% dans les mêmes conditions que précédemment.

Filtrer sur creuset alundum R A 98 et sous vide; laver 5 fos à l'eau bouillante.

Sécher à l'étuve à 103° pendant 15 heures; peser; calciner au four à 700° pendant 2 heures et peser; la différence entre ces deux pesées, multipliée par 100, donne la teneur en cellulose %.

Nous sommes donc très loin de la méthode publiée par la Station de Weende; mais la méthode de Weende, ainsi modifiée par neutralisations, présente l'avantage, d'une part, de supprimer des centrifugations et des lavages ce qui constitue un gain de temps appréciable et, d'autre part, de donner des résultats plus reproductibles, ce qui lui assure une plus grande précision. Notre méthode a d'ailleurs été adoptée par les Laboratoires du Ministère de l'Agriculture en Espagne.

RÉSUMÉ

La méthode de dosage de la cellulose proposée comporte une neutralisation après chaque attaque. Elle présente les avantages suivants: suppression de lavages et de centrifugations, d'où un gain de temps, et obtention de résultats plus reproductibles, d'où une plus grande précision.

SUMMARY

The proposed method for the estimation of cellulose includes a neutralisation after each attack. This method has the advantage of abolishing washings and centrifugations, thus saving time, and that of ensuring more reproducible results and thereby greater precision.

ZUSAMMENFASSUNG

Die vorgeschlagene Methode zur Bestimmung von Zellulose enthält eine Neutralisation nach jedem Aufschluss. Sie hat folgende Vorteile: Ausschaltung von Waschungen und Zentrifugationen, daraus resultiert ein Zeitgewinn, und besser reproduzierbare Resultate, was eine grössere Präzision bedeutet.

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A PROCEDURE FOR THE DETERMINATION OF RADIOACTIVITY DUE TO FISSION PRODUCT NIOBIUM

by

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Since fission product niobium is one of the most important γ-ray emitters in irradiated uranium which has not had a very considerable cooling time, the rapid and accurate determination of its activity is of importance. A rapid radiochemical procedure involving solvent extraction of the niobium has, therefore, been developed. Among the various solvents, which have recently been shown to extract niobium under various conditions, have been ketones (MILNER AND WOOD[1]; STEVENSON AND HICKS[2]; WERNING, HIGBIE, GRACE, SPEECE AND GILBERT[3]; HICKS AND GILBERT[4]; WERNING AND HIGBIE[5]), amines (LEDDICOTE AND MOORE[6]; ELLENBURG, LEDDICOTE AND MOORE[7]), aliphatic phosphoric acids (SCADDEN AND BALLOU[8]), tri-*n*-butyl phosphate (MORRIS, WAIN AND FLETCHER[9]), and di*iso*-butylcarbinol (MOORE[10]). Tri-*n*-butyl phosphate (TBP) has been employed in the new radiochemical procedure for fission product niobium, since it is a very stable, readily available, solvent and almost completely extracts niobium under suitable conditions.

In the new procedure, the first oxalic acid and bromic acid destruction stage of the well known method of GLENDENIN[11] has been used, to get a separation of niobium activity from the bulk of the rest of the fission products. The niobium is then further purified by TBP extraction from HF-H_2SO_4 solution, followed by precipitation as niobic acid by ammonia. The precipitate is washed, ignited, and weighed as Nb_2O_5.
The procedure, with instructions for the radiochemical analysis of uranyl nitrate solutions is given below.

Preparation and standardization of carrier

The carrier is prepared and standardised by the method of GLENDENIN[11], *viz:*

Preparation

Dissolve 26.0 g of potassium niobate in ca. 200 ml of water, heat the solution nearly to boiling and add 15 ml of conc. HNO_3 slowly with stirring. Continue heating and stirring for two to three minutes and centrifuge. Wash the precipitate three times with centrifugation, with 50 ml of hot 2% NH_4NO_3 solution. Add 200 ml of saturated oxalic acid, and heat with stirring until the niobic acid dissolves. Cool and dilute to 1 litre. Filter the solution if it is not clear.

Standardization

Pipette exactly 5 ml of the carrier solution into a 100 ml beaker. Add 30 ml of $6M$ HNO_3 and *ca.* 1g of $KClO_3$ and carefully heat the solution to boiling. Boil gently with occasional stirring for *ca.* 5 minutes. Cool the mixture and add conc. NH_4OH with stirring to make the pH value 8 to 10 (ca. 15 ml). Filter quantitatively on a Whatman No. 42 filter paper through a 2 inch 60° funnel, returning the first portion of the filtrate if it is not clear, and wash with hot water. Ignite in a porcelain crucible at *ca.* 800° C for 15 minutes and weigh as Nb_2O_5.

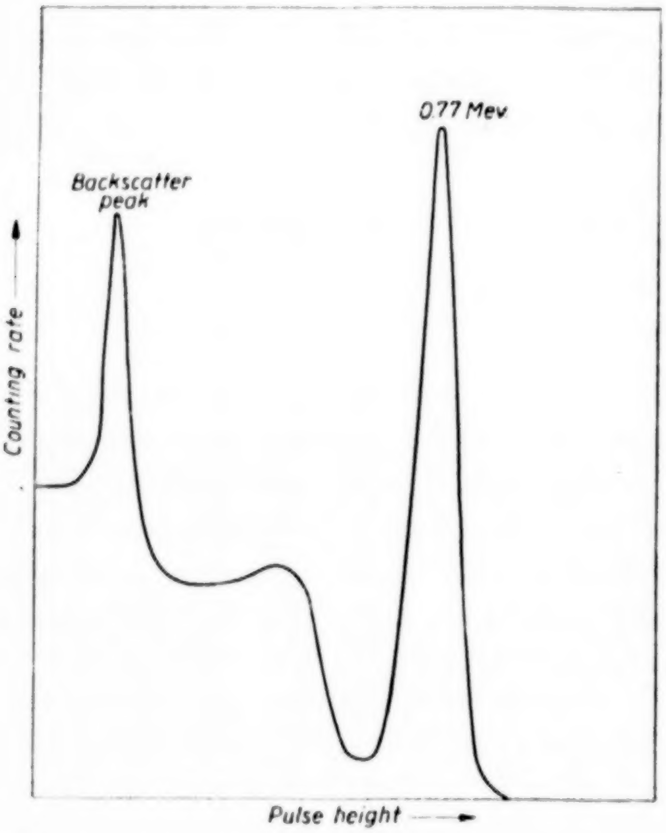

Fig. 1. γ-ray spectrum of Nb_2O_5 sample from the analysis of 99d. cooled uranium, on NaI(Tl) spectrometer.

Procedure (for uranyl nitrate solutions)

Step 1. Place the sample solution (1 to 10 ml volume) in a 50 ml glass centrifuge tube. Add 10 mg zirconium carrier (10 mg Zr/ml prepared from zirconyl nitrate and $1M$ nitric acid).

Step 2. Add to the solution an equal volume of concentrated HNO_3, 1 ml of saturated oxalic acid, and 2 ml of niobium carrier. Gently stir for 10 minutes (*Note* 1). Heat the solution nearly to boiling and add 0.5 g of $KBrO_3$ in small portions, boiling for a few seconds after each addition. Evaporate the solution to low bulk and centrifuge the precipitated niobic acid (*Note* 2). Decant and discard the supernate. Wash the precipitate in 10 ml of hot 2% NH_4NO_3 solution (*Note* 3).

Step 3. Transfer the precipitate to a polythene tube. Dissolve in 2.5 ml of 40% HF, add 2 ml of $12M$ H_2SO_4 and 4-5 ml of pure TBP. Stir mechanically for 2 minutes using a polythene stirring rod. Centrifuge, transfer the organic layer to a clean polythene tube, and discard the aqueous phase. Add 5 ml of petroleum ether to the TBP phase and then 4 ml of $6M$ NH_4OH. Stir the phases for 1 minute. Centrifuge at high speed for 1 minute and separate and discard the organic layer. Wash the aqueous phase with 5 ml of petroleum ether (*Note* 4). Centrifuge at high speed for 1 minute, decant and discard the organic and aqueous supernate.

Step 4. Wash the niobic acid precipitate with 10 ml of hot 2% NH_4NO_3 solution. Transfer to a crucible with 2 ml of distilled water, heat to dryness, and ignite at 800° C for *ca.* 15 minutes. Allow to cool in a desiccator, and break up the Nb_2O_5 to a fine powder with a flat-ended glass rod. Slurry the Nb_2O_5 with a little ethyl alcohol on to a weighed aluminium counting tray. Dry under a radiant heater lamp taking care to ensure that the resulting deposit on the tray is uniform. Weigh the tray and Nb_2O_5 to establish the chemical yield. Count on a γ-scintillation counter through a standard aluminium-lead sandwich.

Notes

1. For exchange of Nb activity and carrier, oxalic acid must be present, and it is advisable to stir the solution for at least 10 minutes.
2. If $[SiF_6]^{-2}$ or F^- is present niobic acid will not be precipitated. Addition of an excess of H_3BO_3 to the sample eliminates this difficulty.
3. The washing is done with 2% NH_4NO_3 solution to prevent peptization.
4. The washing with petroleum ether is designed to remove any traces of TBP.

Reagents

Conc. nitric acid.
Saturated oxalic acid.
Potassium bromate.

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2% Ammonium nitrate (slightly acidified with nitric acid).
40% Hydrofluoric acid.
12*M* Sulphuric acid.
Tri *n*-butyl phosphate.
Petroleum ether.
Ethyl alcohol.

DISCUSSION

The procedure was tested for separation from different possible interfering activities by using the following radioactive tracers: caesium 137 - barium 137 (equilibrium mixture), cerium 144 - praseodymium 144 (equilibrium mixture), ruthenium 106 - rhodium 106 (equilibrium mixture), molybdenum 99- technetium 99m (equilibrium mixture), and zirconium 95. The results of these experiments are summarized in Table I. These data indicate that separation from caesium, cerium, praseodymium, ruthenium, rhodium, molybdenum, technetium, and zirconium is adequate for fission product mixtures normally encountered.

TABLE I

SEPARATION OF VARIOUS ELEMENTS IN THE PROCEDURE

Element	*γ activity added*		*γ activity above background in counted samples*		
Cs-Ba	176000	cts/min.	15	34	cts/min.
Ce-Pr	75000		1	0	
Ru-Rh	356000		20	19	
Mo-Tc	68600		45	121	
Zr	79100		120	69	(values uncorrected for growth of Nb activity during the experiment)

Analyses by the procedure of four uranyl nitrate solutions prepared from neutron irradiated uranium which had cooled various lengths of time were carried out. Results are given in Table II.

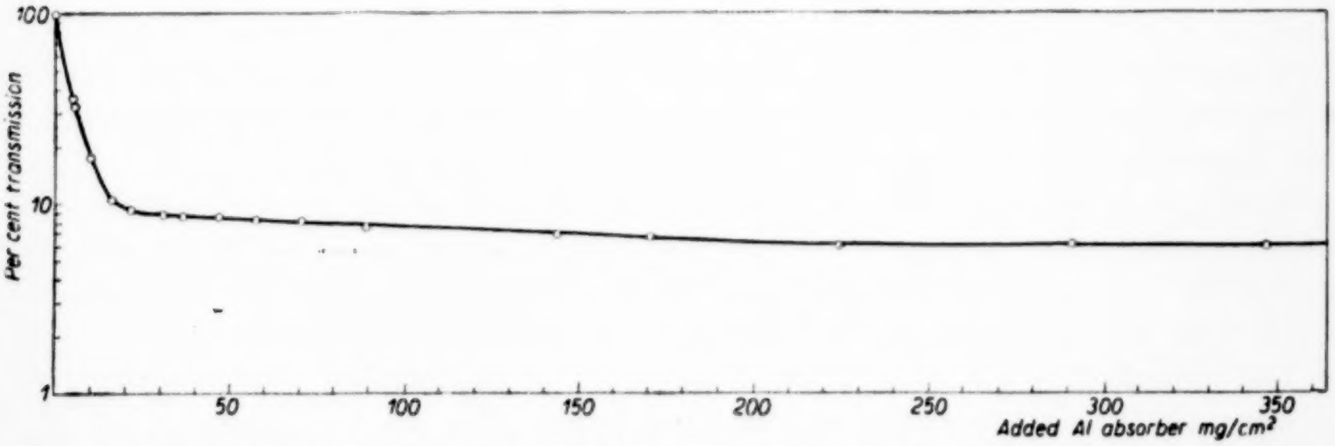

Fig. 2. Aluminium absorption curve of Nb_2O_5 sample from the analysis of 99d. cooled uranium.

Aluminium absorption curve measurements and γ-scintillation spectrometer measurements indicated the presence of a β-particle of *ca.* 0.15 Mev. and a γ-ray of 0.77 Mev. in each case. These results agree well with the values of 0.160, 0.159, 0.148, 0.146, and 0.15 Mev. quoted for the 35d. niobium-95 β-particle and the values of

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TABLE II

RADIOCHEMICAL NIOBIUM ANALYSES OF URANYL NITRATE SOLUTIONS PREPARED FROM IRRADIATED URANIUM COOLED FOR VARIOUS LENGTHS OF TIME

Solution	*Days since end of irradiation*		*Niobium activity γ cts/min/ml*	
			1894	
			1900	
1	10		1976	
			1864	
		mean	1909	$s = 2.5\%$
			5867	
			6019	
2	99		5898	
			5898	
		mean	5920	$s = 1.1\%$
			3540	
			3510	
3	146		3510	
			3660	
		mean	3555	$s = 2.0\%$
			3505	
			3444	
4	150		3496	
			3466	
		mean	3478	$s = 0.8\%$

$s = \sqrt{\frac{\Sigma d^2}{n-1}}$ = standard deviation, where d = deviation from the mean of single measurements. n = number of measurements.

0.745, 0.758, 0.77 and 0.75 Mev. quoted for the energy of the niobium-95 γ-ray (HOLLANDER, PERLMAN AND SEABORG[12]). No other β or γ activities could be detected in samples from Solutions 2, 3 and 4, save a trace of a β component of energy *ca.* 0.7 Mev.* In the case of samples obtained on Solution 1 in which the uranium had had only 10d. cooling, aluminium absorption curve measurements and γ-scintillation spectrometer measurements indicated the presence of contamination due to tellurium activity. γ-scintillation counter measurements of the decay curves of the samples indicated a maximum contamination of *ca.* 5%.

It can be stated from the above results that the procedure provides satisfactory radiochemical purity with γ-scintillation counting using a standard Al-Pb sandwich, and also a standard deviation of 2% or less, in the analysis of material with a cooling time of greater than 30 days (Te interference is then negligible).

The procedure is quick, requiring about 1.5 h for a complete analysis. Chemical yields generally obtained have been of the order of 60%.

The interchange between tracer and carrier under the conditions of the procedure has been tested by taking a portion of pure niobium-95 tracer in 1M nitric acid

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* It should be noted that the Al absorption curve of pure 35 d. ^{95}Nb is not obtained until about two weeks after the last step in any radiochemical procedure for the activity analysis of niobium in mixed fission products. This is due to the presence of conversion electrons from the decay of 90 h. ^{95m}Nb.

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solution, which was evaporated on a tray and γ counted; the same quantity of tracer was analysed by the radiochemical procedure. The results shown in Table III indicate that satisfactory exchange occurs.

TABLE III

ANALYSIS OF CARRIER FREE NIOBIUM TRACER BY THE METHOD

	TBP procedure	evaporated sample
γ activity of niobium	4018 cts/min	3925 cts/min
corrected for 100% yield	4052	

ACKNOWLEDGMENTS

Thanks are due to Mr. L. SALMON for carrying out some of the γ-scintillation spectrometer measurements and to Mr B. J. LAUNDY for helping to test the procedure.

SUMMARY

A procedure using tri-*n*-butyl phosphate solvent extraction has been devised and investigated for the determination of the activity due to fission product niobium. The method gives good radiochemical purity and a standard deviation of 2% or less, except on material which has had a very short cooling time since the end of neutron irradiation.

RÉSUMÉ

Un procédé, utilisant le phosphate de *n*-butyle comme solvant d'extraction, a été proposé et mis au point pour la détermination de l'activité du niobium (produit de fission). Cette méthode permet d'obtenir une bonne pureté radiochimique et une déviation standard de 2% au moins, sauf pour le matériel qui a eu un temps de refroidissement très court après la fin de l'irradiation de neutrons.

ZUSAMMENFASSUNG

Es wird ein Verfahren vorgeschlagen das *n*-Butylphosphat als Extraktionsmittel verwendet, und für die Bestimmung der Aktivität des Spaltproduktes Niob ausgearbeitet wurde. Diese Methode gestattet eine gute radiochemische Reinheit und eine Standardabweichung von mindestens 2% zu erhalten, ausgenommen für das Material, welches eine sehr kurze Erkaltungszeit nach der Neutronenbestrahlung hatte.

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SÉPARATION DE TRACES DE FLUORURE DES SELS D'ALUMINIUM(III) PAR ÉCHANGEURS D'IONS

par

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Les méthodes de dosage des fluorures (gravimétries, volumétries et colorimétries) échouent en présence de Al(III). Une séparation préalable est nécessaire.

Habituellement on sépare par:

— Distillation du fluorure de silicium, qui nécessite de grandes précautions manipulatoires. Cette méthode ne convient pas en présence d'ions Al^{+3} (voir par exemple[1]).

— Solubilisation des fluorures par attaque au moyen du carbonate de sodium fondu. Un peu d'aluminium(III) passe en solution et fausse le dosage ultérieur des ions fluorhydriques[2].

— Distillation de l'acide silicifluorhydrique[3]. C'est la méthode la plus utilisée. Les ions complexant les fluorures gênent également. Des améliorations ont été proposées[4]. En particulier, LACROIX[5] obtient une séparation quantitative pour des rapports fluorure/aluminium supérieurs ou égaux à 1. Pour des rapports inférieurs à 1, la séparation cesse d'être quantitative.

HONDA[6] propose une séparation au moyen de résines échangeuses d'ions en milieu acide. Nous avons repris les essais de cet auteur et nous proposons une séparation en milieu alcalin à l'aide d'une résine échangeuse d'anions. On peut ainsi séparer jusqu'à 100 p.p.m. de fluorure dans Al(III).

I. SÉPARATION EN MILIEU ACIDE

En solution acide, l'aluminium existe principalement à l'état d'ions Al^{+3} et le fluorure sous forme d'acide fluorhydrique HF.

En éluant une solution d'aluminium(III) et de fluorure préalablement fixée au sommet d'une colonne de résine échangeuse de cations, on peut espérer éluer rapidement l'acide fluorhydrique qui ne se fixe pas sur la résine.

Après de nombreux essais, nous avons trouvé que les meilleures conditions opératoires sont les suivantes:

Résine: Amberlite I.R. 120 tamisée de façon à ne conserver que les grains ayant un diamètre de 0.3 mm.
Colonne: hauteur 30 cm, diamètre 8 mm.
Vitesse d'écoulement: 2 ml/minute.
Solution éluante: acide chlorhydrique de titre compris entre 0.01 et 0.5*N*.

Le fluorure est dosé sur des fractions de 10 ml par le nitrate de thorium; en utilisant du nitrate de thorium 0.01M, on peut encore doser 100 microgrammes de fluorure.

Résultats

Pour des quantités initiales de fluorure et d'aluminium données, la fraction de fluorure recueillie dans un volume d'éluant déterminé est indépendante de l'acidité de la solution, entre 0.01 et 0.5N.

Dans le Tableau I nous rassemblons les résultats obtenus pour une solution initiale contenant 2 mg d'aluminium (III) et 10 mg de fluorure, l'acidité de la solution éluante étant 0.1N.

TABLEAU I

volume élué (ml)	*fluorure trouvé %*
100	93
120	95
160	97
200	98

De plus, pour une acidité et un volume d'éluat fixés, lorsque le rapport Al/F augmente, la fraction de fluorure trouvée diminue. Ainsi pour une concentration d'acide chlorhydrique 0.1N et pour des quantités d'aluminium et de fluorure toutes deux égales à 10 mg, on ne retrouve que 80% du fluorure dans 200 ml d'éluat.

Les complexes cationiques formés entre Al(III) et F^- sont donc trop stables et trop fortement fixés sur la résine pour permettre une séparation quantitative en particulier lorsqu'il s'agit de traces de fluorure.

II. SÉPARATION EN MILIEU ALCALIN

En milieu alcalin, l'aluminium et le fluor existent respectivement sous forme d'ions AlO_2^- et F^-. S'il est possible de trouver des conditions (nature de la résine, hauteur de colonne, débit, concentration des réactifs) pour que les coefficients de partage des deux ions soient suffisamment différents et le nombre de plateaux théoriques[7] suffisamment grand, on peut espérer effectuer une séparation par élution à l'aide d'une résine échangeuse d'anions.

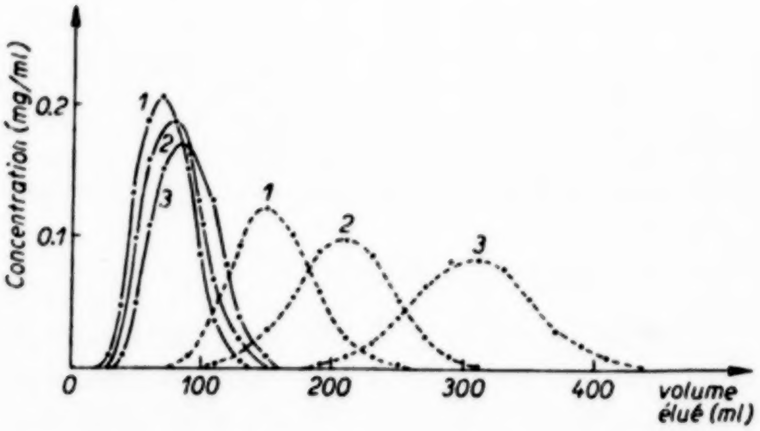

Fig. 1. Courbes d'élution de 10 mg d'aluminium ou de fluorure sur une colonne de 27 cm.
Courbes 1 : Solution éluante : NaOH 0.4N
„ 2 : „ „ : „ 0.3N
„ 3 : „ „ : „ 0.2N
—·—·— Aluminate - - - - - - Fluorure

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Sur la Fig. 1, sont représentées les courbes obtenues avec une colonne de 27 cm de hauteur pour une quantité totale d'aluminium(III) ou de fluorure égale à 10 mg et pour diverses concentrations de soude de la solution éluante. Les conditions opératoires exactes sont indiquées ci-dessous.

On constate que la séparation n'est quantitative qu'avec une solution de soude 0.2*N* et que la zone où les deux courbes ne se chevauchent pas n'est que de 10 ml.

Nous avons refait les mêmes essais avec une colonne de hauteur double (54 cm). Les résultats sont indiqués Fig. 2. Cette fois la zone libre est importante (environ 80 ml avec la soude 0.2*N*) et la séparation est quantitative.

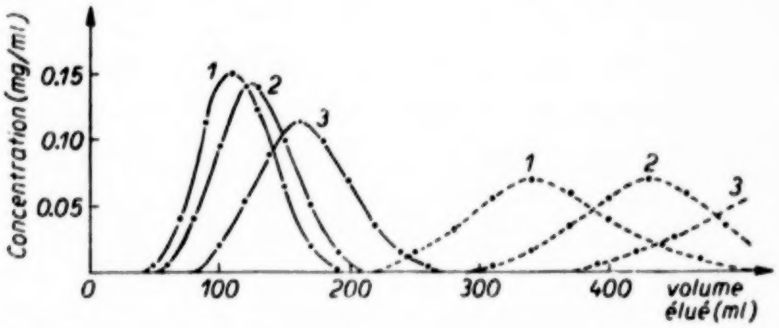

Fig. 2. Courbes d'élution de 10 mg d'aluminium ou de fluorure sur une colonne de 54 cm.
Courbes 1 : Solution éluante : NaOH 0.4*N*
„ 2 : „ „ : „ 0.3*N*
„ 3 : „ „ : „ 0.2*N*
—·—·— Aluminate - - - - - - Fluorure

1) *Mode opératoire*

Nous proposons le mode opératoire suivant pour la séparation du fluorure contenu dans l'aluminium(III) à des teneurs variant de 50% à 0.01%.

Préparation de la colonne. Peser environ 30 g d'Amberlite I.R.A. 400 tamisée de façon à ne conserver que les grains de 0.3 mm de diamètre. Laisser une nuit dans l'eau distillée. Remplir une colonne de 1 cm² de section. La hauteur de résine est de 54 cm. Faire passer 100 ml de soude 2*N*, laver avec 100 ml d'eau distillée. Saturer la résine en faisant passer 100 ml de soude 0.2*N*. Le débit de ces solutions étant de 2 à 2.5 ml/minute.

Préparation des solutions. La solution d'aluminate est préparée par attaque d'un poids connu d'aluminium à 99.9% par une solution de soude dans un creuset de nickel. La solution de fluorure est obtenue par dissolution d'une quantité connue de fluorure de sodium préalablement séché à 110°.

Elution. Faire passer 50 ml de solution (contenant 100 mg d'Al(III) et au minimum 10 microgrammes de fluorure) sur la colonne à la vitesse de 2 à 2.5 ml/min. Eluer ensuite à la même vitesse l'aluminium(III) avec une solution de soude 0.2*N* jusqu'à ce que le volume recueilli soit de 280 à 300 ml. Eluer enfin le fluorure avec une solution de soude *N*. Recueillir 100 ml dans le cas des traces et 250 ml pour les quantités importantes de fluorure (supérieures ou égales à 10 mg).

2) *Dosage du fluorure par spectrophotométrie*

Pour les quantités supérieures à 1 mg, la méthode de LACROIX ET LABALADE[5] est utilisée: on détermine la diminution de densité optique d'une solution du complexe ferrisulfosalicylique à laquelle est ajoutée la solution de fluorure. Précision 1%.

Pour les quantités inférieures à 1 mg on utilise la méthode de MEGREGIAN[8]: on détermine la diminution de densité optique d'une solution contenant le composé formé par le zirconium et l'ériochrome-cyanine R. Précision 5%. Limite de sensibilité 2 μg/100 ml.

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Résultats. Nous rassemblons dans le Tableau II les résultats de l'analyse, après séparation de 100 mg d'aluminium(III) et de différentes quantités de fluorure.

TABLEAU II

Quantités de fluorure (mg)		*Erreur %*
Prévue	*Trouvée*	
10	9.9	−1
10	10.05	+0.5
1	0.98	−2
1	1.02	+2
0.01	0.0095	−5
0.01	0.011	+10

RÉSUMÉ

On propose une méthode de séparation du fluorure d'aluminium(III) par chromatographie au moyen d'un échangeur d'anions en milieu alcalin. La méthode est valable jusqu'à la limite inférieure de 100 p.p.m. de fluor dans l'aluminium.

SUMMARY

A method is proposed for the separation of aluminium(III) fluoride by chromatography by means of an anion exchanger in alkaline medium. The method is applicable to a minimum of 100 p.p.m. of fluoride in the aluminium.

ZUSAMMENFASSUNG

Es wird eine Methode vorgeschlagen zur Abtrennung von Aluminium(III)-fluorid durch Chromatographie mittels eines Anionenaustauschers in alkalischem Milieu. Die Methode ist gültig bis zu einer unteren Grenze von 100 p.p.m. Fluor im Aluminium.

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THE SEPARATION AND ESTIMATION OF HEXA- AND PENTAVALENT MOLYBDENUM BY PAPER CHROMATOGRAPHY

by

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INTRODUCTION

Investigations in progress on the role of molybdenum in the nutrition of higher plants and micro-organisms showed the need to develop methods for the separation of molybdenum compounds in different valency states, with a view to their application to biological systems. Tentative methods at present under investigation include partition between immiscible solvents, chromatographic separation on paper or on columns, and electrodialysis.

This paper reports the separation by descending paper chromatography, and the quantitative estimation of the hexa- and pentavalent molybdenum compounds in a thiocyanate system. Some of the results obtained in the preliminary stages of the work are also included.

EXPERIMENTAL

Preliminary investigations

Molybdenum solutions. The preliminary work included experiments on the separation of molybdenum, as molybdate, from lower valency states present after reduction of a molybdate solution in 25 % v/v sulphuric acid by zinc dust to the wine-red colour stage. This solution contains mainly pentavalent molybdenum[1] but further reduction produces a lower, possibly trivalent state[2]. The final concentrations were arranged to contain about 6,000 μg Mo per ml and 5 μl spots were used, *i.e.* 30 μg Mo. Mixtures of the two valency states were obtained either by superimposing separate additions to the same spot on the paper, or by using a single spot of a mixed solution of the valencies.

Treatment of paper: Whatman No. 1 chromatographic paper, 20 cm in width was employed. This was washed by soaking for 1 hour in 2*N* HCl followed by rinsing 20 times with glass distilled water[3]. This treatment was essential to remove contamination, mainly by iron. It was found that treatment of the paper by an 0.1% solution of ethylenediaminetetraacetic acid (EDTA) as the disodium salt, pH 8.0, resulted in abnormal chromatographic behaviour of the molybdenum compounds which spread irregularly over the paper. Descending chromatography was used throughout; ascending chromatography was tried, but was found to be unsatisfactory.

Solvent systems and effects of EDTA: Solvent mixtures which consisted of aqueous solutions of potassium thiocyanate mixed with relatively non-polar components, *e.g.* *iso*-butyl alcohol, *iso*-amyl alcohol, acetone or ethyl acetate, were tested initially. Separations under these conditions were better at low temperatures (around 1° C) compared with those done at room temperatures (20° C), but tended to be incomplete, owing to marked forward or backward 'tailing' of the hexa- or pentavalent molybdenum zones respectively. For these reasons the non-polar constituent was omitted from the solvent and an aqueous thiocyanate system which contained a weak acid was used. Acetic acid was found to be the most satisfactory; propionic, formic or hydrochloric acids gave inferior separations when introduced into the system.

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In all the above solvent systems pentavalent molybdenum(Mo^{V}) travelled ahead of hexavalent (Mo^{VI}). The aqueous acetic acid-thiocyanate systems were unable to separate pentavalent molybdenum from a lower valency state and a method for doing this is described by one of us (H.M.S.) in a later paper.

The inclusion of 0.1% EDTA in the molybdenum solutions prevented the formation of molybdenum blue in mixtures under near-neutral conditions, or on the paper when the spots dried. Neither the inclusion of EDTA in solvent systems nor, as described above, in the molybdenum solutions achieved any improvement in the separations and EDTA was therefore omitted from the solvent system finally adopted. The molybdenum blue produced temporarily by successive additions of hexa- and pentavalent molybdenum solutions to the paper was decomposed as the thiocyanate containing solvent travelled over the spot.

Quantitative separation and estimation

Preparation of molybdenum standards: A stock standard Mo^{VI} solution was prepared by dissolving 1.875 g of freshly ignited AnalaR molybdenum trioxide in a minimum volume of warm sodium hydroxide solution, which was then acidified with hydrochloric acid, and diluted to 100 ml with distilled water. This solution contained 12,500 μg Mo^{VI} per ml; other Mo standard solutions were prepared from the stock solution by dilution.

A standard solution of Mo^{V} was prepared by warming 5 ml of diluted Mo^{VI} stock solution which contained 500 μg of Mo per ml with 5 g of potassium thiocyanate and 10 ml of 5*N* hydrochloric acid to 50° - 60° C. All the molybdenum was reduced to Mo^{V} thiocyanate after 10-15 minutes. The solution was then diluted to 100 ml with a 10% solution of potassium thiocyanate in 2*N* hydrochloric acid and filtered.

Molybdenum was estimated colorimetrically as the pentavalent thiocyanate compound in ethyl acetate. 5 ml aliquots of the standard Mo^{V} thiocyanate solution were shaken with different volumes of redistilled ethyl acetate and the extracts filtered. A Hilger Spekker absorptiometer was used to measure the colour intensities obtained in relation to pure ethyl acetate. A drum setting of 1.300 was used with 1 cm cells and Ilford No. 603 blue-green filters.

Chromatographic procedure: Quantitative separations between Mo^{VI} and Mo^{V} as their thiocyanates on paper chromatograms were obtained with a solvent system which consisted of water, 100 ml; acetic acid, 10 ml; potassium thiocyanate, 10 g. R_F values were 0.3 - 0.4 for Mo^{VI}, and 0.8 - 0.9 for Mo^{V}. The chromatograms were prepared using the pilot-strip technique[4]. Then, 0.10 - 0.20 ml of acidified molybdate solution, which contained 625 μg Mo^{VI} per ml was delivered along the starting line of the main part of the chromatogram followed by a similar volume of a Mo^{V} thiocyanate solution which contained 550 μg Mo^{V} per ml in 10% potassium thiocyanate in 2*N* hydrochloric acid. A separate spot of the mixture was run alongside the main part of the chromatogram on an attached pilot-strip. After a run of about 20 cm in the eluant the pilot-strip was cut off and sprayed with a mixed solution of 10% stannous chloride and potassium thiocyanate, or with a solution of dithiol[5], followed by exposure to hydrochloric acid fumes, in order to determine the positions of the separated molybdenum valency bands on the main chromatogram without spraying the latter. If the molybdenum concentration is not too low the pilot-strip is not essential as the bands can be revealed by exposing the paper to hydrochloric acid fumes. The elution was carried out at normal room temperature (20° C); if performed at lower temperatures (1° C) inferior separations were obtained (*cf.* preliminary experiments with organic solvent systems). The molybdenum bands were cut out and disintegrated by shaking with 30 ml of 10% potassium thiocyanate in 2*N* hydrochloric acid. The mixture was heated to 40°-45° C for 10 minutes, cooled and shaken with 10 ml of redistilled ethyl acetate. The ethyl acetate extract was then separated by centrifugation, filtered if necessary, and the colour intensity measured on the calibrated Hilger Spekker.

The results of some typical experiments are given in Table I.

TABLE I

EXAMPLES OF RECOVERIES OF HEXA- AND PENTAVALENT MOLYBDENUM AFTER CHROMATOGRAPHIC SEPARATION

Expt No.	*μg* Mo^{VI} *taken*	*μg* Mo^{VI} *recovered*	*μg* Mo^{V} *taken*	*μg* Mo^{V} *recovered*
1	125	127.5	—	—
2	125	127.5	—	—
3	—	—	109	110
4	—	—	147	143
5	69	71.5	60	59.5
6	62.5	69.5*	55	55.5
7	62.5	67*	55	54.5
8	66	67	55	54

* Trace of iron present in the ethyl acetate extract.

It is necessary to avoid prolonged contact between molybdate and strongly acid thiocyanate solutions as this causes error due to the production of pentavalent molybdenum.

Extraction of the molybdenum from the paper by means of boiling water in a Soxhlet apparatus gave low recoveries. Attempts to digest the paper containing the molybdenum by means of a sulphuric-perchloric acid mixture also resulted in low values. This may have been due to the volatilization of a lower valency chloro-compound of molybdenum. Preliminary treatment of the bands by alkali-hydrogen peroxide mixtures did not prevent this loss, although in other work (to be reported), this procedure was used during the destruction of organic material to prevent loss of molybdenum present in a lower valency state. The addition of stannous chloride to the initial extracts of the paper before further extraction with ethyl acetate also caused low readings. Hence a warm mixture of potassium thiocyanate and hydrochloric acid is recommended in order to achieve quantitative extraction of the molybdenum compounds and the reduction of the hexavalent state to the pentavalent.

The amount of molybdenum which could be detected visually on the chromatogram was less than 10 *μg*.

ACKNOWLEDGEMENT

One of us (M.I.C.) wishes to thank the Spanish Consejo Superior de Investigaciones Científicas for a Maintenance Grant which enabled him to participate in this work at Long Ashton Research Station.

SUMMARY

Preliminary investigations were made upon the chromatographic separation of hexa- and pentavalent molybdenum by organic solvent systems which contained potassium thiocyanate. A method for the quantitative separation of these valency states by paper chromatography in a water-acetic acid-potassium thiocyanate eluant is described. The estimations were performed colorimetrically as molybdenum pentathiocyanate which was extracted into ethyl acetate. As little as 10 μg Mo can be detected in the respective valency states. The probable error of the quantitative estimation is of the order of ± 3% for 50-100 μg Mo.

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RÉSUMÉ

Des recherches préliminaires ont été effectuées sur la séparation chromatographique du molybdène (VI) et (V) au moyen d'un solvant organique renfermant du thiocyanate de potassium. Une méthode est décrite pour la séparation quantitative de ces deux stades de valence par chromatographie sur papier au moyen d'un éluant, formé d'eau, d'acide acétique et de thiocyanate de potassium. On dose par colorimétrie le pentathiocyanate de molybdène extrait par l'acétate d'éthyle. On peut déceler jusqu'à 10 µg Mo. L'erreur est de l'ordre de 3% pour 50 à 100 µg Mo.

ZUSAMMENFASSUNG

Es wurden Vorversuche ausgeführt über die chromatographische Abtrennung von Molybdän (VI) und (V) mittels eines organischen Lösungsmittels, welches Kaliumthiocyanat enthält. Es wird eine Methode beschrieben über die quantitative Abtrennung dieser zwei Valenzstadien mit Papierchromatographie durch ein Elutionsmittel, bestehend aus Wasser, Essigsäure und Kaliumthiocyanat. Man dosiert das Molybdänpentathiocyanat, welches mit Äthylacetat ausgezogen wurde, kolorimetrisch. Man kann bis zu 10 µg erfassen. Der Fehler schwankt in der Grössenordnung von 3% für 50-100 µg Mo.

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THE PAPER CHROMATOGRAPHIC SEPARATION OF AMMONIUM CHLORIDE, HYDRAZINE, HYDROXYLAMINE, PHENYLHYDRAZINE AND PHENYLHYDROXYLAMINE

by

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INTRODUCTION

During the course of work on the paper chromatographic separation of inorganic ammine complexes and lower metallic valency states, the R_F values of ammonium chloride and some organic reducing agents were determined and a separation of ammonium chloride, hydrazine, hydroxylamine, phenylhydrazine and phenylhydroxylamine was obtained. Both upward and downward chromatography were used, the former being more convenient for smaller quantities or simple mixtures.

EXPERIMENTAL

Apparatus

For downward runs, the all-glass apparatus consisted of a trough (24 cm long, 2.5 cm diameter) supported by a stand contained in a tank covered with a ground glass plate. Saturation of the atmosphere of the tank by the solvent vapour was obtained using a dish of solvent in the bottom and a second trough of solvent on the stand.

For upward runs, the apparatus consisted of a gas jar 30 cm high and 7.5 cm internal diameter. The top of the gas jar was greased and covered with two pieces of glass (side by side) 14 × 5 cm and a cover plate 14 × 9 cm. 75 ml of solvent mixture were added, and the gas jar was well shaken. In order to prevent solution of the grease in the solvent, the solvent was not allowed to reach the top of the jar. The plates were pulled apart by about 1 mm and the filter paper strip (with the spots containing the mixture to be separated) was inserted until the lower end of the paper just touched the solvent surface. The cover plate was placed over the protruding upper end of the strip and elastic bands were passed over the ends of the glass slides and cover plate (Fig. 1). The paper strip was left in position until the solvent had advanced *ca.* 15 cm and was then removed, dried and sprayed.

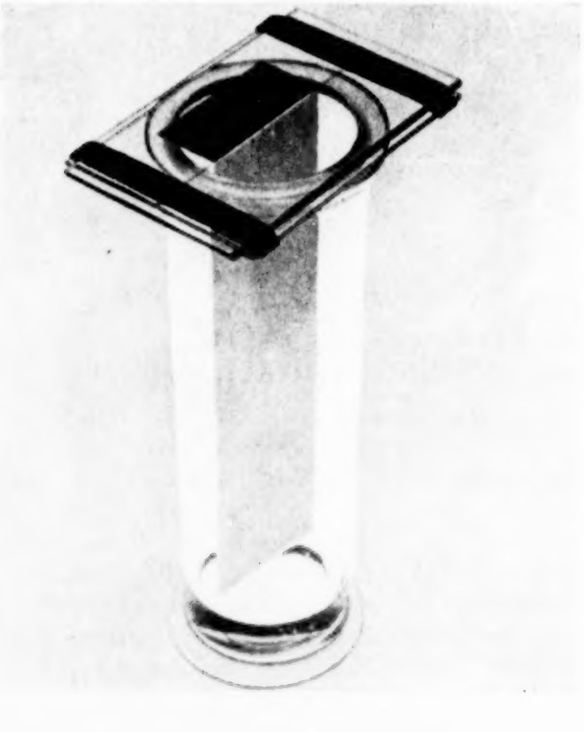

Fig. 1

Solvent, preparation of the paper, and spray reagents

The most satisfactory solvent was:
15 ml water, 4 ml 'A.R.' concentrated hydrochloric acid, 50 ml diethyl ether and 30 ml methyl alcohol (free from formaldehyde).

To minimize esterification of the alcohol, the cooled components were mixed in the order given. The solvent was always freshly prepared and, before admission, the temperature of the solvent was adjusted to the temperature of the chromatographic vessel. See reference[1] for previous use of this solvent.

Acid-washed Whatman No. 1 paper was used for the separations and was prepared as follows[2]: The ready-cut sheets were placed in $2N$ HCl (A.R.) for four days and then washed free of chloride ions with about ten successive washings of distilled water. The acid-washing of the first four days was improved by regular agitation, *e.g.* every few hours. Finally, to remove chloride ions completely, for the last few washings the distilled water was changed every hour.

This process removes all but traces of the iron, magnesium and calcium in the paper and improves the compactness of the spots.

The ammonium ion was located by spraying with lead cobalt nitrate solution followed by saturated aqueous sodium nitrite solution[3]. The background colour of the chromatogram was removed by washing with distilled water. This reagent also detects potassium, which occurs at R_F 0.13.

Hydrazine, hydroxylamine and their derivatives were detected with a spray of 0.5% (w/v) picryl chloride in ethyl alcohol, followed by drying and holding over ammonia[4]. A complete separation of N_2H_4, NH_2OH, $C_6H_5.NH.NH_2$ and $C_6H_5.NH.OH$ is obtained with a 15 cm run, but NH_2OH is not separated from NH_4Cl unless a longer run (25–30 cm) is carried out. The colours given below are obtained when the sprayed chromatogram is held over ammonia, while the colours given in brackets develop after the chromatogram has been withdrawn from the ammonia. If the acid is not allowed to evaporate from the paper before spraying, different colours are again obtained.

TABLE I

Compound	R_F	*Colour*
$NH_2.CO.NH.NH_2$	0.22	red (purple-brown)
N_2H_4	0.23	deep blue (purple-brown)
NH_4Cl	0.36	grey
NH_2OH	0.42	orange-brown
$C_6H_5.NH.NH_2$	0.65	grey-brown (red-brown)
$C_6H_5.NH.OH$	0.81, 0.95	dark brown

Without spraying, N_2H_4, $C_6H_5.NH.NH_2$ and $C_6H_5.NH.OH$ can be seen under ultra-violet light as fluorescent or dark spots. If the sprayed chromatogram is held over ammonia and viewed under ultra-violet light, the dark spots show up clearly against the fluorescent yellow-green background (Fig. 2).

Notes on the separation

(a) To obtain R_F values reproducible to within 0.02, it was necessary to standardize the experimental conditions carefully as follows (although perfectly satisfactory separations are obtainable using simplified procedures):

1. Direction of solvent flow — downward elution.
2. Type and treatment of the paper — see previous section.
3. Length of run — 25 ± 5 cm.
4. Temperature — 18 ± 1°C.
5. Concentration of solutions: NH_4Cl — $\frac{M}{2}$ aqueous,

   $N_2H_4.2HCl$, $NH_2.OH.HCl$, $C_6H_5.NH.NH_2.HCl$,

   $C_6H_5.NH.OH$ — $\frac{M}{5}$ aqueous,

   $NH_2.CO.NH.NH_2$ — $\frac{M}{10}$ aqueous.

6. Distance of starting line from solvent level — 3 cm.
7. Time of equilibration of the tank — 2 days.
8. Time of equilibration of the paper (*i.e.* length of time the strip is in contact with, and is able to absorb, the solvent vapour before running the chromatogram). This time was zero, so that no oxidation of $C_6H_5.NH.OH$ took place.
9. Diameter of the spots and whether wet or dry — 7 mm approx. 0.002 ml; dry.

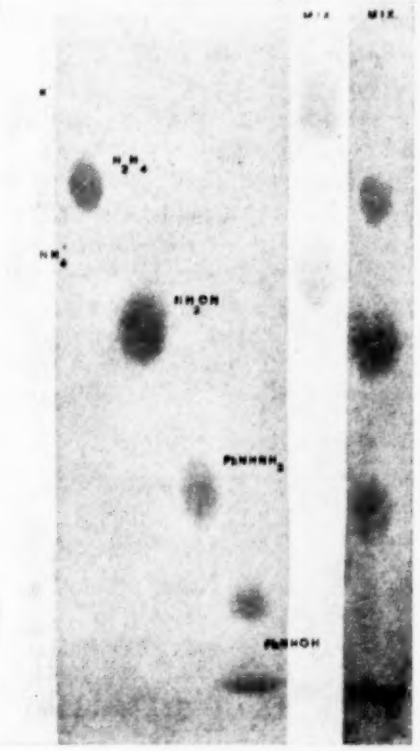

Fig. 2

(b) The chief remaining sources of error arise from the difficulty of reproducing acid-washed paper of similar properties, and from the fact that the equilibration of the tank is disturbed on admitting the strip. When compounds to be separated are not liable to decompose on the paper, then this latter difficulty is overcome by fully equilibrating the paper during equilibration of the tank.

(c) One factor of importance which is often overlooked concerns the distance of the starting line from the solvent level in the trough. If an undried chromatogram is sprayed with dilute blue litmus solution, it is found that the R_F value of the acid-front is 0.83. If one component of the solute mixture dissolves completely in the organic region between the acid and solvent fronts, then only one spot ($R_F > 0.83$) will be obtained. If, however, part of the component is eluted by the purely organic solvent, and the rest by the solvent behind the acid-front, then two spots will result. This would explain the double-spotting of the compounds phenylhydroxylamine (R_F 0.81 and 0.95) and *p*-nitrophenylhydrazine (R_F 0.70 and 0.97). The size of the lower spot increases with distance of starting line from the solvent level in the trough. This appears to be due to a corresponding increase in the width of the acid-free region passing over the starting line. One of the advantages of upward chromatography is that it is easier to place the spots at a known distance close to the solvent level. A technique for downward chromatography has been devised by D. J. JONES of these laboratories for eliminating this double-spot phenomenon by introducing the solute mixture to the strip when the second phase boundary has passed the starting line.

(d) When the phenylhydroxylamine solution has been allowed to stand, it produces further spots which are due to decomposition products, for instance, a red-brown spot for *p*-aminophenol at R_F 0.67.

SUMMARY

The paper chromatographic separation of ammonium chloride, hydrazine, hydroxylamine, phenylhydrazine and phenylhydroxylamine is accomplished using the solvent system: 50 parts by volume diethyl ether, 30 parts methyl alcohol, 15 parts water and 4 parts concentrated hydrochloric acid. A double-spot phenomenon is described which depends upon the distance of the starting line from the solvent level.

RÉSUMÉ

La séparation chromatographique sur papier du chlorure d'ammonium, de l'hydrazine, de l'hydroxylamine, de la phénylhydrazine et de la phénylhydroxylamine est effectuée à l'aide du solvant suivant: 50 parties (en volume) d'éther éthylique, 30 parties d'alcool méthylique, 15 parties d'eau et 4 parties d'acide chlorhydrique concentré. Un phénomène de double-tache est décrit, dépendant de la distance de la ligne de départ d'avec le niveau du solvant.

ZUSAMMENFASSUNG

Die chromatographische Trennung auf Papier von Ammoniumchlorid, Hydrazin, Hydroxylamin, Phenylhydrazin und Phenylhydroxylamin wurde mit Hilfe des folgenden Lösungsmittels ausgeführt: 50 Teile (Volumen) Äthyläther, 30 Teile Methylalkohol, 15 Teile Wasser und 4 Teile konzentrierte Salzsäure. Es wird ein Erscheinen von Doppelflecken beschrieben, das von der Distanz Ausgangslinie-Lösungsmittelniveau abhängt.

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SÉPARATION NIOBIUM-TANTALE
CONTRIBUTION À L'ÉTUDE DE L'ÉLECTROPHORÈSE SUR PAPIER*

par

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I. INTRODUCTION

La séparation du niobium et du tantale dans un mélange des deux éléments a été intensivement étudiée ces dernières années. Les méthodes chimiques comme celle de SCHOELLER[1], employant le tannin comme réactif, et celle de MARIGNAC[2] basée sur la cristallisation fractionnée des complexes fluorhydriques, ne donnent guère satisfaction dans tous les cas. Par contre, des résultats satisfaisants ont été obtenus en appliquant les méthodes chromatographiques. Ainsi la séparation des deux éléments a été réalisée sur Dowex-2 par KRAUS ET MOORE[3], HUFFMAN[4] et SPEECKE[5], en employant soit des complexes fluorhydriques, soit des complexes oxaliques, tandis que BURSTALL[6] et MERCER ET WELLS[7] ont obtenu par chromatographie de partition sur la cellulose des résultats comparables pour des complexes fluorhydriques. Dans un article précédent, nous avons décrit la séparation des complexes oxaliques par chromatographie sur papier[8].

Une séparation des deux éléments basée sur leurs propriétés électrochimiques n'a pas été essayée jusqu'ici. Nous nous sommes proposés d'étudier cette séparation par électrophorèse sur papier.

II. CONDITIONS GÉNÉRALES DE TRAVAIL

Description du montage

L'étude des différentes méthodes d'électrophorèse sur papier, décrites dans la littérature, permet de les grouper en trois catégories distinctes: au premier groupe appartiennent toutes les méthodes dans lesquelles le ruban de papier est suspendu verticalement, les deux moitiés plongeant dans les solutions tampons, et formant un angle qui peut varier entre des limites très larges. C'est la méthode employée par DURRUM[9], GORDON[10], WUNDERLY[11] et autres chercheurs. Dans le second groupe nous classons les méthodes dans lesquelles le papier est suspendu horizontalement, comme l'ont décrit WIELAND[12] et McDONALD[13].

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* Recherches exécutées sous les auspices de l'Institut Interuniversitaire des Sciences Nucléaires.

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Dans le dernier groupe nous rangeons les autres méthodes dans lesquelles le papier est placé horizontalement entre deux plaques de verre. Nous retrouvons ce principe chez CREMER ET TISELIUS[14], KUNKELL ET TISELIUS[15], ROBBINS ET RALL[16] et autres.

Abstraction faite de la plus grande résistance exigée du papier on peut s'attendre, pour les deux premières méthodes, à une répartition inhomogène de l'électrolyte tampon le long du papier, entraînant une variation du gradient de potentiel et, en conséquence, une vitesse de migration des ions variant le long du ruban.

Dans les expériences décrites ci-dessous, nous avons fait usage d'un montage suivant le principe de CREMER ET TISELIUS, mais légèrement simplifié. L'appareil est représenté dans la Fig. 1. Il est entièrement en plexiglas et mesure 36 sur 16 cm, la hauteur étant 10 cm. Il est muni d'une plaque formant couvercle, permettant de travailler en chambre close saturée de vapeur d'eau.

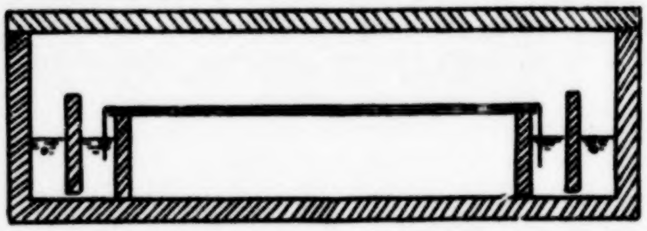

Fig. 1. Appareil pour l'électrophorèse.

La largeur de la chambre permet de faire à la fois trois essais sur trois rubans de papier de 3 cm de largeur, placés parallèlement dans l'appareil.

Les deux parois supportant la plaque de verre avec le papier sont distantes de 30 cm, permettant l'emploi de bandes d'une longueur effective de 30 cm. Contrairement à l'usage général de placer le papier entre deux plaques de verre, nous n'employons qu'une plaque. Le rôle essentiel de la seconde plaque étant d'éviter l'évaporation de la solution dans le papier, nous avons trouvé dans quelques essais préliminaires qu'en travaillant en chambre bien saturée, les résultats n'étaient pas influencés en omettant la plaque supérieure.

Pour éviter la diffusion des produits d'électrolyse dans le papier, les deux compartiments contenant l'électrolyte tampon sont divisés par un diaphragme, terminant à 1.5 mm du fond

Les électrodes sont placées horizontalement sur toute la largeur de l'appareil, dans les compartiments extrêmes. Entre les deux électrodes nous appliquons une différence de potentiel constante, règlée par voie potentiométrique. Le courant est mesuré au moyen d'un milliampèremètre.

Préparation des rubans de papier

Whatman No. 1 a été employé dans toutes les expériences. Trois bandes identiques, largeur 3 cm, longueur 42 cm, ont été employées en parallèle dans chaque essai, permettant de juger de la reproductibilité des résultats.

Après avoir marqué le centre du ruban d'un léger trait, le papier est trempé pendant 30 sec dans la solution tampon. L'excès de solution est enlevé au moyen d'un morceau de papier filtre. Le ruban humide est placé ensuite dans la chambre d'électrophorèse sur la plaque de verre support, ses deux extrémités plongeant dans la solution tampon. Une petite quantité (40 λ) de la solution à analyser, contenant 10 à 50 γ de chaque élément, est portée ensuite au centre de la bande, soit en appliquant 4 fois une quantité de 10 λ en 4 points différents marqués le long du trait, soit en effleurant le papier le long du trait indiqué avec la pointe de la pipette, répétant cette opération 4 fois avec un volume de 10 λ à chaque reprise. On obtient ainsi une zone de départ homogène et étroite.

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Détection du Nb et du Ta

Dans toutes les expériences le Ta a été détecté par voie radiochimique* en utilisant l'isotope ^{182}Ta. A défaut d'un isotope de Nb nous avons employé pour la détection de cet élément la réaction colorimétrique au pyrogallol.

Nous procédons de la façon suivante: après mise en évidence de la zone niobique par réaction colorimétrique, on indique sa position sur le ruban qui est ensuite découpé en petits morceaux de 1 cm de longueur. La mesure de l'activité du ^{182}Ta dans chaque morceau permet de déterminer la position du Ta.

Pour des mesures plus précises et quantitatives nous avons déterminé d'abord l'activité du ^{182}Ta le long du ruban coupé en pièces de 0.5 cm. Chaque morceau est ensuite élué au moyen d'une solution tampon Na_2SO_3 — $NaHSO_3$. On ajoute une quantité déterminée d'une solution à 30% de pyrogallol et on mesure l'extinction de la solution du complexe formé au spectrophotomètre Beckman B, pour la longueur d'onde 3650 Å, utilisant comme blanc une solution du réactif.

Préparation des solutions

Deux solutions différentes de Nb et de Ta ont été employées, notamment des solutions de complexes citriques et de complexes oxaliques, obtenues à partir des oxydes Nb_2O_5 et Ta_2O_5 purs. Pour la préparation de ces complexes nous avons suivi exactement le mode opératoire décrit dans un article précédent[8].

Pour les solutions tampons nous n'avons employé que des produits pour analyse ou très purs. Le pH des solutions a été déterminé au moyen du potentiomètre Cambridge, avec une électrode de verre.

III. SÉPARATION DU Nb ET DU Ta SOUS FORME DE COMPLEXES CITRIQUES

HAISSINSKY[17] a déterminé la stabilité des complexes citriques et oxaliques de Nb et de Ta en fonction du pH. Ses résultats sont indiqués dans le Tableau I.

TABLEAU I

pH DE PRÉCIPITATION DE Nb ET DE Ta DE LEURS SOLUTIONS COMPLEXES

	oxalates + NaOH		*citrates + KOH*	
	début	*fin*	*début*	*fin*
Nb	4.9	5.2	8.2	9.0
Ta	4.0	6.3	11.6	12.4

L'étude de ce tableau montre qu'il y a un intervalle de pH dans lequel le complexe citrique du Ta restant stable, celui du Nb se décompose avec précipitation de l'hydroxyde. Règlant le pH de la solution tampon employée à une valeur comprise entre 9 et 11.5 on pouvait espérer maintenir le Nb précipité en place, tandis que les ions complexes du Ta pourraient migrer sous l'influence du champ électrique.

Des essais entrepris dans ce but, utilisant des solutions tampons $Na_2CO_3+Na_2B_4O_7$, d'un pH variant de 9.2 à 11 n'ont pas donné le résultat espéré. Le Ta se répartit sur toute la longueur du demi ruban à partir du centre, présentant cependant un maximum assez net situé à une distance du centre d'autant plus grande que le pH est plus élevé. Contrairement à nos prévisions le Nb se déplace également, formant une zone relativement étroite coïncidant avec le front de la zone du Ta.

D'autres essais ont été entrepris, basés, d'une part sur la dissociation des complexes en milieu acide citrique, d'autre part sur la stabilité relative des complexes citriques et oxaliques des deux éléments. Nous avons employé dans ce but respectivement des solutions tampon acide citrique + citrate de potassium de pH variant de 2.02 à 7.81 et des solutions d'acide oxalique + oxalate d'ammonium de pH 2.14 à 5.76.

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* Nous remercions ici Mlle UYTTERHAEGEN qui s'est chargée des mesures de la radioactivité des centaines d'essais.

Les résultats sont entièrement comparables à ceux obtenus avec la solution au tétraborate: il y a superposition de zones pour les deux éléments, tandis que la distance de migration augmente avec le pH. La zone du Nb est plus étalée.

IV. SÉPARATION DU Nb ET DU Ta SOUS FORME DE COMPLEXES OXALIQUES

Tenant compte des pH de précipitation des complexes oxaliques trouvés par HAISSINSKY (Tableau I), nous serons limités à des valeurs de pH moins élevées pour les solutions tampons employées.

Trois solutions tampons différentes ont été essayées:

$(HCOO)_2 + (NH_4)_2C_2O_4$:

Toutes les solutions employées étaient 0.25*M* en oxalate tandis que la concentration en acide oxalique variait de 0 à 0.25*M*. Une solution d'acide oxalique pur 0.25*M* a également été essayée. Le pH variait de 5.76 pour l'oxalate à 2.14 pour l'acide. La différence de potentiel entre les électrodes était de 200 V, la durée d'électrophorèse de 2 h.

Aucune solution n'a permis la séparation des 2 éléments. Comme pour les complexes citriques il y a superposition des zones. Cependant, contrairement à ce que nous avons trouvé là, la vitesse de migration diminue quand le pH augmente. Nous devons remarquer cependant que la variation de la force ionique des solutions n'est certainement pas sans influence. D'autre part toutes les solutions employées sauf l'oxalate pur et l'acide pur, ont donné deux maxima bien distincts pour le Ta.

Nous avons représenté dans la Fig. 2 le résultat obtenu avec une solution tampon de pH 4.46. La zone niobique a été hachée.

La présence de deux zones distinctes semble indiquer que le Ta existe sous forme de deux ions complexes tantalo-oxaliques différents. Ce problème intéressant n'a pu être traité jusqu'ici.

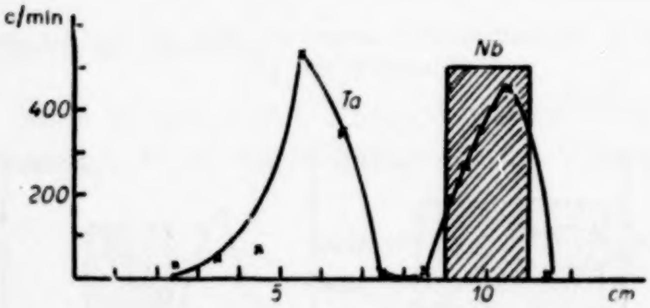

Fig. 2. Déplacement de Nb et de Ta. Solution tampon: $(COOH)_2 + (NH_4)_2C_2O_4$, pH 4.46.

Acide citrique + Na_2HPO_4

Des solutions tampons citriques - phosphatiques de pH variant de 4.6 à 5.8 ont été préparées suivant les indications de McILVAINE[18].

La concentration totale des solutions est relativement constante. Avec ces solutions, l'électrophorèse a été poursuivie pendant 3 h 30′ avec une différence de potentiel aux électrodes de 200 V.

Comparant les résultats obtenus avec les différentes solutions, nous constatons que la vitesse de migration augmente en fonction du pH comme c'était le cas pour les complexes citriques. Aussi il n'y a plus qu'une seule zone pour le Ta. La séparation obtenue varie en fonction du pH et passe par un optimum pour la solution de pH = 5.4.

Avec cette solution le Nb se retrouve dans une zone très étroite, mais la séparation est rendue difficile du fait que la zone du Ta présente un élargissement assez prononcé.

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Dans la Fig. 3 le résultat obtenu avec cette solution a été représenté.

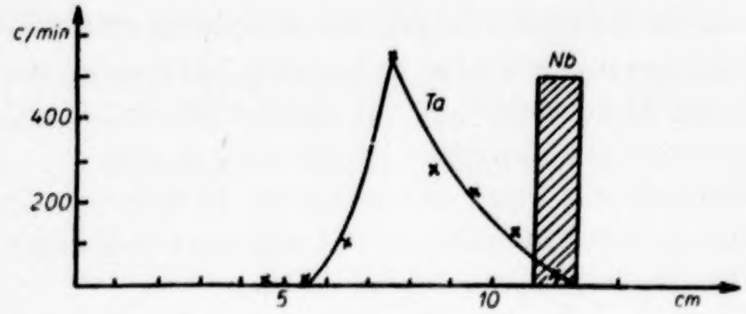

Fig. 3. Déplacement de Nb et de Ta. Solution tampon: acide citrique + Na_2HPO_4, pH 5.4.

Acide citrique - citrate de potassium

Nous avons remplacé dans la solution tampon précédente le phosphate de sodium par le citrate de potassium. Les quantités d'acide citrique et de citrate ont été variées de façon à obtenir des solutions de force ionique constante, égale à 0.6, et de pH variant de 2.09 pour l'acide pur, à 6.81 pour la solution de citrate. Une solution de force ionique double a également été essayée. L'électrophorèse a été poursuivie pendant 3 h avec une différence de potentiel aux électrodes de 200 V.

Après détection des zones nous avons déterminé pour les différentes solutions employées les distances parcourues respectivement par le maximum de la zone tantalique et le centre de la zone niobique, mesurées à partir du centre du ruban — point de départ. Les valeurs moyennes de trois essais avec chaque solution sont reproduites dans la Fig. 4. La distance verticale entre les deux courbes est une mesure de la séparation obtenue. Nous voyons que celle-ci sera optima entre les valeurs de pH 3.2 et 3.4 et qu'elle diminue tant pour les solutions de pH inférieur que pour celles de pH plus élevé. En outre pour la solution acide (pH 2.09) le Ta est réparti sur toute la largeur du ruban. La zone niobique devient également très large, de même que dans la solution de citrate (pH 6.81). La situation des zones a été représentée dans la Fig. 5. Nous voyons qu'une séparation complète des deux éléments est obtenue moyennant les solutions tampons de pH 3.20 à 3.40, tandis que pour des valeurs de pH inférieures et supérieures la séparation devient moins satisfaisante. Pour les valeurs extrêmes il y a superposition complète.

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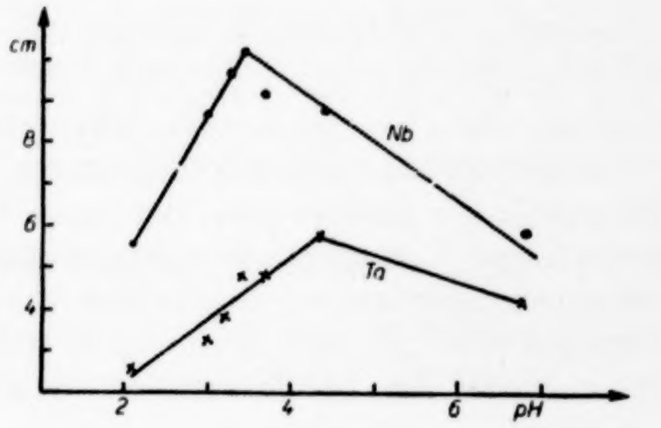

Fig. 4. Situation des zones de Nb et de Ta en fonction du pH.

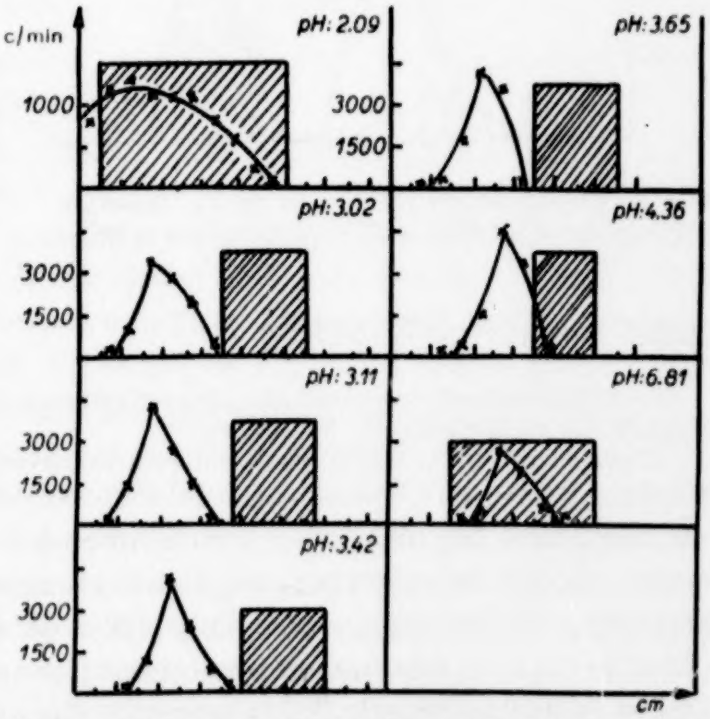

Fig. 5. Déplacement de Nb (hachuré) et de Ta (courbe). Solution tampon: acide citrique + citrate de K.

Nous avons pu constater également que l'augmentation de la force ionique de la solution tampon de 0.6 à 1.2 diminue de façon appréciable la vitesse de migration et la distance entre les zones à séparer.

Des essais ont été entrepris avec la solution citrique de pH 3.42 afin d'améliorer la séparation obtenue en déplaçant la zone initiale vers l'extrémité négative du ruban et en prolongeant la durée de l'électrophorèse.

La comparaison des résultats obtenus avec ceux obtenus en partant du centre, permet de formuler les faits suivants:

1. La vitesse de déplacement des ions dans le papier est plus grande du côté de l'électrode négative que du côté de l'électrode positive.
2. La vitesse de déplacement diminuant, la distance parcourue par les ions n'est pas proportionnelle au temps d'électrophorèse.
3. La séparation obtenue en partant de l'extrémité du côté de l'électrode négative est moins satisfaisante qu'en partant du centre, même après un temps double et une distance parcourue beaucoup plus grande. Ce fait est dû surtout à l'élargissement de la zone tantalique.

Ces résultats nous ont conduit à étudier plus profondément les différents facteurs jouant un rôle dans la séparation des ions par électrophorèse sur papier. Il serait intéressant en effet de déterminer des conditions telles que le déplacement des ions soit proportionnel au temps, ce qui permettrait d'améliorer la séparation par simple augmentation de la durée d'électrophorèse.

V. ÉTUDE DES DIFFÉRENTS FACTEURS INFLUENÇANT LA SÉPARATION DES IONS PAR ÉLECTROPHORÈSE SUR PAPIER

Relations générales

Nous savons que les ions d'une solution, sous l'influence d'un champ électrique uniforme F, se déplacent avec une vitesse v_i donnée par la relation:

$$v_i = u_i\,F = \frac{Z_i\,e_0 F}{300.6\,\pi\eta\,r_i}\ \text{cm/sec} \quad \ldots\ldots\ldots \quad (1)$$

dans laquelle u_i = la mobilité de l'ion i
Z_i = le nombre de charges élémentaires e_0
r_i = le rayon de l'ion migrant
η = la viscosité de la solution.

La distance parcourue en un temps t sera:

$$d_i = v_i\,t = u_i\,F\,t \quad \ldots\ldots\ldots\ldots \quad (2)$$

Si nous plongeons dans la solution deux électrodes distantes de L cm et si nous appliquons entre les électrodes une différence de potentiel de E volts, nous obtenons:

$$d_i = u_i\,t\,\frac{E}{L} = u_i\,t\,\frac{iR}{L}$$

où i est l'intensité du courant et R la résistance de la colonne. Substituant R par sa valeur en fonction de la conductivité de la solution et des dimensions de la colonne, nous obtenons:

$$R = \frac{1}{\varkappa}\frac{L}{s} \text{ et } d_i = \frac{u_i\, t\, i}{\varkappa \cdot s} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

Il s'en suit que la distance parcourue par un ion donné est proportionnelle à l'intensité du courant appliqué et inversement proportionnelle à la valeur des facteurs s et $\varkappa$. L'augmentation de $\varkappa$ diminuera en même temps u_i par augmentation de la viscosité η et de la valeur effective du courant i causant la migration des ions à séparer.

Quand nous appliquons l'électrophorèse sur une bande de papier, d'autres facteurs interviennent et le phénomène devient plus compliqué. Nous devons tenir compte d'abord d'un courant d'électro-endosmose résultant, sous l'influence d'un champ électrique appliqué, dans un déplacement de la solution à vitesse constante dans une direction dépendant de la charge du papier — ordinairement négatif.

D'autre part la solution monte dans le ruban des deux côtés, avec une vitesse décroissante à partir des réservoirs d'électrolytes vers le centre du papier, et dépendant du degré de saturation de ce dernier. Après saturation ce courant de liquide ne sert plus qu'à compenser la perte par évaporation.

Il s'en suit qu'une particule chargée partant du centre sous l'influence du champ électrique avec une vitesse d'électrophorèse constante, sera entraînée en sens inverse par un courant liquide dont la vitesse augmente vers les extrémités du ruban. La particule viendra au repos à un point où les deux vitesses seront égales. Partant d'une extrémité le déplacement sous l'influence du courant liquide s'ajoute à la migration par électrophorèse, devient 0 au centre, puis prend le signe inverse.

PUCAR[19], DE WAEL[20] et MACHEBOEUF[21] ont étudié intensément ces phénomènes. Tenant compte du courant d'électro-endosmose et des courants de saturation MACHEBOEUF a calculé pour la distance parcourue par une particule chargée à partir d'un point x_0 et dans un temps t, la relation suivante:

$$x - x_0 = \frac{(\varepsilon - kx_0)\,(1 - e^{-kt})}{k}$$

où ε est la vitesse d'électrophorèse de la particule sous l'influence du champ appliqué, et k une constante dépendant de la vitesse d'évaporation.

Il a montré que tous les autres facteurs tenus constants, la particule viendra au repos en un même point, indépendamment du point de départ. Ce point d'équilibre ne dépend que de la vitesse d'électrophorèse et d'évaporation et est donné par la relation

$$x_E = \frac{\varepsilon}{k}$$

Plusieurs conclusions importantes découlent immédiatement de ces considérations:

1. Pour obtenir une séparation proportionnelle au temps d'électrophorèse il faudra tâcher de déplacer le point d'équilibre vers l'infini. Dans ce but il faut réduire au minimum le courant de saturation. A cet effet:

a) on ne commencera l'électrophorèse qu'après saturation complète du papier.

b) on évitera tant que possible l'évaporation pendant l'électrophorèse.

Travaillant en chambre close saturée, l'évaporation sera fonction de la température ambiante et de la chaleur produite dans le ruban sous l'influence du courant imposé.

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On calcule pour la chaleur dégagée par cm² de surface:

$$G = 0.24 \frac{i^2 \, t}{\varkappa \cdot s}$$

Aussi nous relatant à la relation (3) on en déduit qu'on aura avantage à diminuer l'ampérage et à augmenter t tenant le produit $i \cdot t = C^t$.

2. La relation (3) montre l'influence de la concentration de la solution tampon ($\varkappa$) ainsi que de la structure du papier. Le facteur s est en effet la section efficace du papier, déterminé par la relation:

$$s = \frac{G_V - G_S}{\delta \cdot L}$$

où G_V est le poids du papier à l'état saturé et G_S le poids du papier sec, δ la densité de la solution et L la longueur du papier. En outre la distance réelle d', parcourue par un ion, n'est pas déterminée par la distance linéaire d entre la position initiale et finale, mais est donnée par la relation:

$$d' = k \, d$$

$k > 1$, étant fonction de la texture du papier employé.

3. A cause de l'évaporation de la solution et du courant de saturation, la concentration de l'électrolyte le long du papier n' est pas constante. Il s'en suit que le potentiel pendant l'électrophorèse n'est pas constant. Il faut le corriger régulièrement, ce qui entraîne une augmentation du courant. En même temps le gradient de potentiel variera le long du ruban, et on ne pourrait attendre un déplacement uniforme des ions. Le contrôle de l'ampérage est alors de première importance.

Dans les expériences suivantes nous avons étudié l'influence de différents facteurs sur la séparation du Nb et du Ta moyennant la solution citrique de pH 3.42.

Nous avons contrôlé d'abord si la relation simple (3) est applicable à condition de tenir compte des courants d'électro-endosmose et de saturation. Ensuite nous avons tâché de réduire ces courants à un minimum et de déterminer des conditions opératoires permettant l'application directe de cette relation.

Étude expérimentale

Pour étudier l'influence des facteurs i, $\varkappa$, s dans le cas de l'électrophorèse sur papier il faut que les courants d'électro-endosmose et de saturation soient nuls, ou reproductibles et constants le long du papier. Comme ce n'est pas le cas en pratique, nous devons tenir compte de leur valeur réelle et corriger les valeurs mesurées des distances parcourues par les ions d'un terme exprimant l'influence de ces courants gênants.

Mesure du courant d'électro-endosmose et de saturation

Le déplacement de la solution dans le papier sous l'influence du courant d'électro-endosmose et de saturation a été déterminé au moyen d'une solution d'arabinose à 1%. Dans ce but le ruban traité à la solution tampon comme de coutume est marqué d'une série de traits distants de 4 cm, à partir du centre. Une petite quantité (10 λ) de la solution d'arabinose est portée sur les différents endroits ainsi indiqués. Pendant l'électrophorèse, les particules de sucre, non chargées, suivent le mouvement de la solution et sont détectées après un temps convenable au moyen d'une solution de phtalate d'aniline[22]. Le résultat obtenu après 3 h d'électrophorèse avec un courant de 4 mA est représenté dans la Fig. 6 a. Chaque point est la moyenne de 3 essais parallèles. Les déplacements sont comptés positifs pour la direction vers l'électrode positive et vice-versa. L'endroit correspondant sur le papier est indiqué en abcisse, mesuré en cm à partir du centre o.

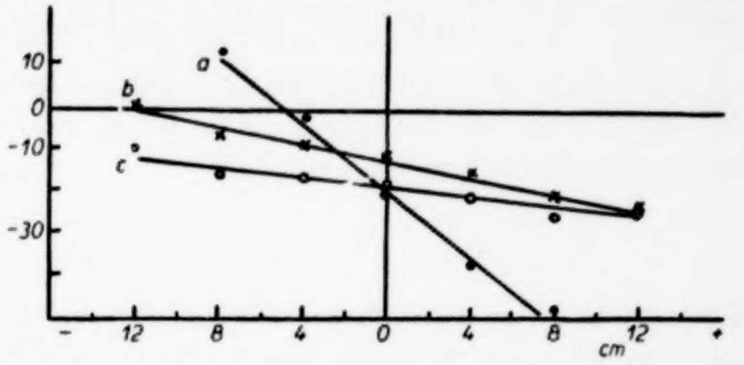

Fig. 6. Courants d'électro-endosmose et de saturation.

Si le courant de saturation est zéro, le courant d'électro-endosmose étant constant sur toute la longueur du papier se traduirait par une droite parallèle à l'abcisse. Nous constatons que ce n'est pas le cas dans les conditions opératoires générales décrites plus haut. L'inclinaison très forte de la droite indique que le courant de saturation est intense aux deux extrémités du papier. Le point d'équilibre est situé du côté de l'électrode négative, indiquant un courant d'électro-endosmose de l'électrode positive à l'électrode négative. Nous avons pu constater également que ces courants sont sujets à des variations assez grandes d'un essai à l'autre.

Dans toutes les expériences ci-dessous nous avons déterminé dans chaque essai les courants d'électro-endosmose et de saturation, pour le centre du papier. Une parallèle menée par le point obtenu à la droite moyenne trouvée pour ces courants dans les mêmes conditions de travail, permet de calculer la correction correspondante au point de départ ainsi qu'au point final.

La moyenne de ces deux valeurs a été appliquée comme correction à la distance parcourue des ions pour obtenir le déplacement par électrophorèse.

Déplacement en fonction du temps sous ampérage et force ionique constants

Une série d'essais a été faite moyennant la solution tampon acide citrique - citrate de pH 3.42 et de force ionique 0.6. L' ampérage fut règlé à 4.5 mA et tenu rigoureusement constant. Les résultats obtenus après 2, 3, 4 et 6 h d'électrophorèse ont montré qu'il n'y a séparation des deux éléments qu'après 6 h. Les distances parcourues ont été mesurées pour le maximum de la bande pour chaque élément. Les résultats obtenus, après correction pour les courants d'électro-endosmose et de saturation, sont représentés dans la Fig. 7, chaque point étant la valeur moyenne de trois expériences. On voit que, dans les conditions choisies il y a linéarité entre le déplacement des ions par électrophorèse et le temps.

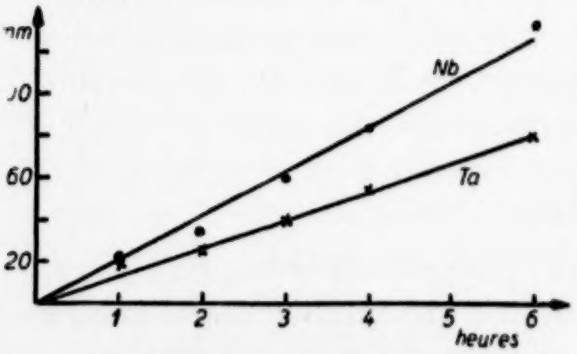

Fig. 7. Déplacement de Nb et de Ta en fonction du temps, sous ampérage et force ionique constants.

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Influence de la concentration de la solution tampon

La résistance de la colonne étant fonction de la concentration en électrolyte de la solution tampon, il fallait pour tenir l'ampérage constant, augmenter le potentiel appliqué. Etant limités dans ce sens, nous avons étudié l'influence de la concentration de l'électrolyte sous produit $i \cdot t$ constant.

Dans une série d'expériences nous avons fait varier les concentrations de l'acide et du citrate de façon à obtenir des solutions à force ionique I respectivement égale à 0.6 — 0.4 — 0.2 et 0.1, le pH des solutions restant constant = 3.42.

L'ampérage variait de 4.5 mA pour la solution à force ionique $I = 0.6$ à 3 mA pour la solution à force ionique $I = 0.1$.

Les résultats obtenus, corrigés pour les courants d'électro-endosmose et de saturation, sont reproduits dans la Fig. 8. Nous pouvons voir qu'entre certaines limites de I la relation (3) est satisfaite. La distance parcourue par les ions augmente quand la concentration de la solution tampon diminue, et la séparation s'accentue. Pour une solution à force ionique $I = 0.2$ le Nb a quitté le papier. D'autre part nous obtenons deux pics dûs au Ta, indiquant qu'à partir de cette concentration d'autres phénomènes interviennent. Pour la plus basse concentration la valeur de migration est telle que nous étions obligés de limiter le temps à 3 h. Il n'y a plus qu'un maximum très vague et les deux éléments sont répartis sur une largeur très grande du papier.

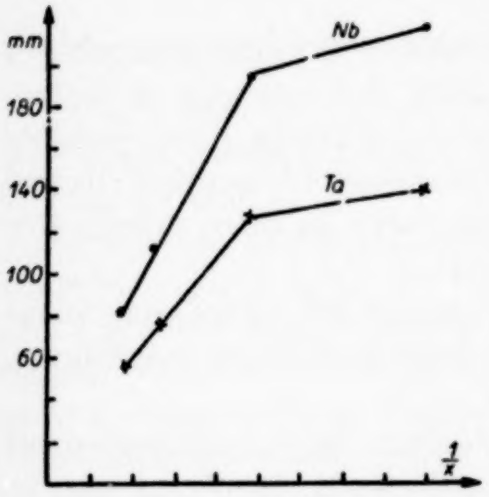

Fig. 8. Déplacement de Nb et de Ta sous produit $i \cdot t$ constant.

Ces résultats indiquent qu'en général il y aura une concentration optimale de la solution tampon, qui devra être déterminée expérimentalement. Cette concentration dans les cas présent est celle correspondante à une force ionique $I = 0.4$.

Influence de l'ampérage

Dans les expériences suivantes nous avons choisi la concentration de la solution tampon telle que $I = 0.4$. Le temps d'électrophorèse est constant = 4 h. Les courants appliqués étaient respectivement 1.5 — 3 — 4 et 4.5 mA.

Jusqu'à la limite supérieure de 4.5 mA, les distances parcourues par les ions, corrigées pour le courant d'électro-endosmose et de saturation, sont proportionnelles au courant appliqué comme on peut le voir dans la Fig. 9.

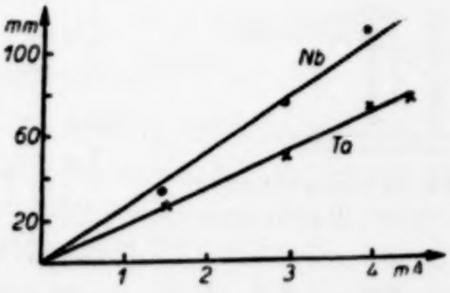

Fig. 9. Déplacement de Nb et de Ta sous temps et force ionique constants.

Influence du point de départ

Dans les conditions optima déduites des expériences précédentes, nous avons tâché de déterminer l'influence du courant de saturation sur la séparation du Nb et du Ta.

Dans ces expériences l'ampérage a été réglé à 4 mA; la force ionique *I* de la solution tampon est de 0.4. Le mélange à séparer est porté sur le papier du côté de l'électrode négative, à 11 cm du centre. Pour deux séries différentes le temps d'électrophorèse était respectivement 4 et 6 h.

Dans ces conditions la distance parcourue par les ions est très grande, mais il en est de même pour la correction pour le courant de saturation. Après correction pour ce dernier, la relation (3) s'applique encore, tenant compte du fait que l'erreur sur la correction devient grande à cause de la variation de celle-ci le long du ruban. La séparation cependant, malgré la distance parcourue, est moins satisfaisante, même après 6 h d'électrophorèse.

Suppression du courant de saturation

Les expériences précédentes ont montré que la relation (3) reste applicable à l'électrophorèse sur papier à condition de tenir compte des courants d'électro-endosmose et de saturation. Si nous arrivons à supprimer ces courants, il sera possible d'améliorer la séparation des deux ions en prolongeant simplement le temps d'électrophorèse. Pour un papier de même longueur, la distance entre les zones pourra être doublée en partant d'une extrémité au lieu du centre.

Pour supprimer le courant de saturation il faut que le papier soit saturé au moment de commencer l'électrophorèse et qu'il le reste pendant toute la durée de l'expérience, c'est-à-dire qu'on évite toute évaporation mesurable.

Nous avons constaté au cours des expériences précédentes, qu'au commencement de l'électrophorèse, l'humidité du papier augmente visiblement, montrant que ce dernier n'est pas saturé. Nous avons essayé d'y remédier de deux façons différentes: soit en portant sur le papier, sur toute sa longueur, une quantité de la solution tampon au moyen d'une pipette; soit en laissant passer le courant d'électrophorèse pendant un certain temps avant de porter le mélange sur le papier. Ce temps de „conditionnement" a été varié de 15 min à 40 min.

L'application du mélange sur le papier après conditionnement se fait par une fente étroite prévue dans le couvercle et normalement couverte d'une petite plaque en plexiglas. Cette technique permet de porter le mélange sur le papier à n'importe quel moment sans influencer la saturation de la chambre.

Les résultats ont montré que les meilleurs résultats sont obtenus en conditionnant pendant 40 min. Dans ces conditions le courant résultant de l'électro-endosmose et de la saturation est représenté par une droite à inclinaison beaucoup plus petite que celle obtenue sans ce conditionnement (Fig. 6b).

Le point d'équilibre est déplacé à 12 cm du centre vers l'électrode négative.

Dans le but de supprimer d'avantage le courant de saturation nous avons essayé la technique représentée dans la Fig. 10.

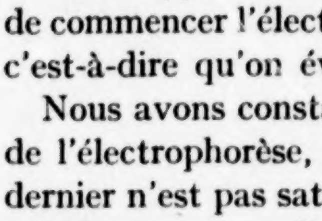
Fig. 10. Schéma du montage avec diaphragme.

Le papier d'électrophorèse A mesure 30 cm et repose sur la plaque de verre. Deux bouts de papier B et B' — de même largeur que A et d'une longueur de 6 cm — plongent d'une extrémité dans le réservoir avec la solution tampon tandis que l'autre extrémité est replié sur le papier central. Le contact direct entre les deux papiers est évité en intercalant une mince feuille de cellophane comme diaphragme. Ce diaphragme

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joue le rôle d'inhibiteur par rapport au courant de saturation, tandis que le courant électrique passe sans difficultés.

La saturation du ruban est réalisée en portant sur celui-ci, au moyen d'une pipette, 1.6 ml de la solution tampon, quantité préalablement déterminée. On conditionne ensuite pendant 40 min pour homogénéiser.

Dans ces conditions la droite représentant le courant d'électro-endosmose et de saturation est devenue à peu près horizontale, située complètement en dessous de la droite 0. (Fig. 6c). Cela signifie qu'à chaque point du papier le liquide se déplace dans le même sens, vers l'électrode négative. Ces conditions s'approchent du cas idéal où nous n'aurions plus que l'électro-endosmose, représentée par une droite horizontale.

Stabilité du gradient de potentiel dans le ruban

La réduction du courant de saturation entraîne nécessairement une répartition plus homogène de la solution tampon dans le papier — et un potentiel plus constant le long du ruban.

Nous avons mesuré la différence de potentiel entre des points équidistants sur toute la longueur du papier. Dans ce but la plaque support pour le papier est pourvue de 14 rainures dans lesquelles nous plaçons des fils de Pt, connectés à un voltmètre de précision. Le contact des électrodes est assuré par légère pression sur le papier au moyen d'une seconde plaque.

Les différences de potentiel entre les différents points ont été mesurées en opérant une fois sous voltage constant, une fois sous ampérage constant. Dans les deux cas nous avons comparé les résultats obtenus d'une part dans les conditions ordinaires, d'autre part, au moyen du montage à diaphragmes, après conditionnement.

Les résultats ont été réunis dans la Fig. 11.

Dans les conditions ordinaires les valeurs mesurées varient le long du papier de façon irrégulière, entraînant un déplacement irrégulier des ions en fonction du point atteint. Après conditionnement et interposition des diaphragmes, les potentiels mesurés sont pratiquement constants. La supériorité de ce mode opératoire est donc manifeste.

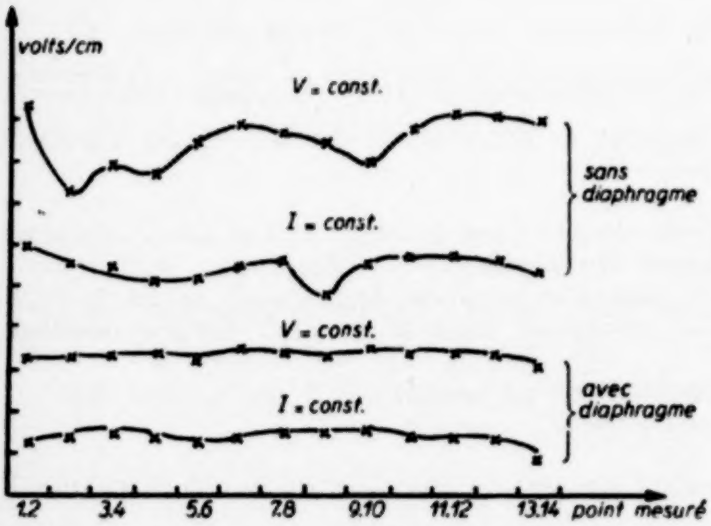

Fig. 11. Variation du gradient de potentiel le long de la bande.

Qualité du papier

Nous avons déjà signalé l'influence du papier figurant de façon implicite dans le facteur *s* de la relation (3). Abstraction faite des considérations ci-dessus, il faut tenir compte également de la résistance au déplacement des ions par frottement, adsorption, *etc.* La distance parcourue par un ion dans le papier sera en réalité donnée par la relation:

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$$d' = d \cdot k \cdot k'$$

où k' est un facteur de résistance, < 1, difficile à déterminer en valeur absolue, mais variant avec les propriétés du papier et entr'autres en fonction de la charge positive ou négative de ce dernier.

La détermination du courant d'électro-endosmose permet souvent de déterminer le choix du papier dans un but déterminé.

Nous avons comparé au Whatman No. 1, employé dans toutes les expériences précédentes, les papiers Whatman No. 3, 31 et 3 MM. Nous avons employé dans ces expériences le montage à diaphragme et l'électrophorèse a été commencée après conditionnement pendant 40 min. La force ionique de la solution tampon était 0.4. L'électrophorèse a été poursuivie pendant 4 h avec un courant de 4 mA.

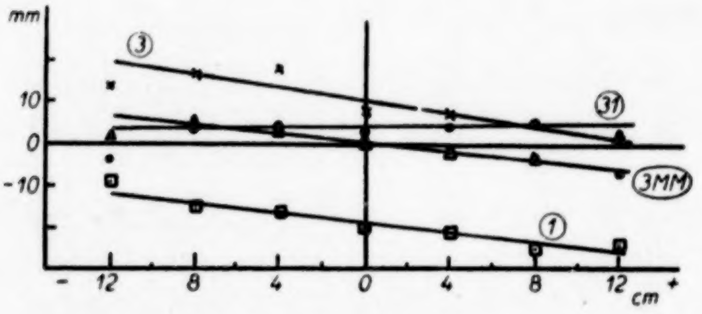

Fig. 12. Courants d'électro-endosmose et de saturation pour différents papiers Whatman.

Dans la Fig. 12 nous avons représenté les courants d'électro-endosmose et de saturation pour les quatre papiers différents. Pour les papiers Whatman 3 MM et 31, le courant de saturation est du même ordre ou même plus faible que pour le Whatman No. 1. Le courant d'électro-endosmose cependant est positif, ce qui signifie, avec la convention adoptée, que les papiers sont chargés positivement. En conséquence, ils seront moins disposés à la séparation d'ions négatifs. La même conclusion vaut à fortiori pour le Whatman No. 3. Aussi, aucun des nouveaux papiers n'a donné une séparation satisfaisante.

Conditions définitives

Tenant compte des résultats de toutes les expériences décrites ci-dessus nous avons établi les conditions définitives suivantes pour la séparation du Nb et du Ta sous forme de complexes oxaliques.

Technique : chambre close, saturée de vapeur, décrite dans le chap. 2. Les électrodes sont placées horizontalement et parallèles à la largeur du papier.

Papier : Whatman No. 1 — bande de 3 cm de largeur et de 30 cm de longueur, suivie de deux bouts de même largeur et de 6 cm de longueur, plongeant dans la solution tampon-montage avec diaphragme.

Solution tampon : acide citrique-citrate de potassium: pH = 3.42
force ionique = 0.4

Intensité du courant : 4 mA (220 V)

Conditionnement : Le papier, étant préalablement imprégné d'une quantité de solution tampon de 1.6 ml est conditionné pendant 40 min.

La solution à analyser est portée sur le papier à l'endroit désiré par une fente préconisée dans le couvercle et normalement fermée pendant l'électrophorèse.

Séparation du Nb et du Ta dans les conditions définitives

Nous avons pu montrer que, dans les conditions indiquées, le courant de saturation est très faible. Il s'en suit un déplacement des ions sensiblement indépendant du [illegible] de départ sur le ruban et une séparation plus satisfaisante en partant de

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l'extrémité négative du ruban et poursuivant l'électrophorèse pendant un temps plus long.

La confirmation de ces conclusions ressort des résultats résumés dans le Tableau II, où les distances parcourues par les ions niobiques et tantaliques sont données respectivement après 4 h d'électrophorèse partant du centre et après 8 h d'électrophorèse partant de 11 cm du centre du côté négatif du ruban.

La Fig. 13 montre la séparation obtenue.

Mobilité des ions

La détermination exacte de la mobilité des ions par mesures d'électrophorèse sur papier est très difficile vu que plusieurs facteurs trop peu connus interviennent.

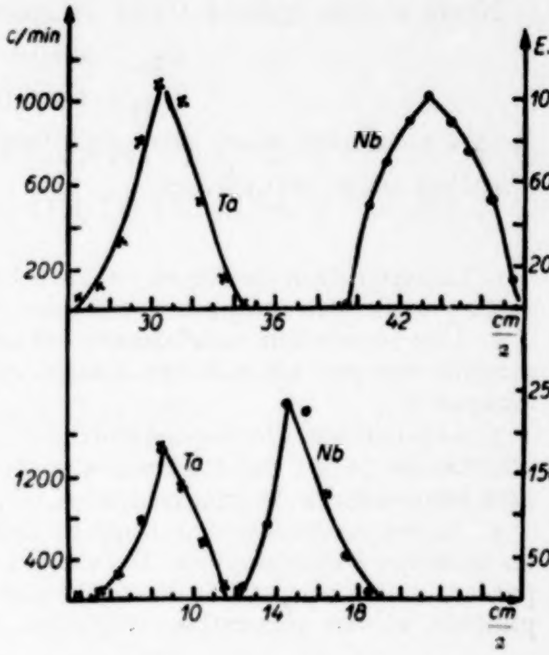

Fig. 13. Déplacement de Nb et de Ta dans les conditions définitives.

TABLEAU II

DÉPLACEMENT DU Nb ET DU Ta DANS LES CONDITIONS DÉFINITIVES

	Distance parcourue	
	Après 4 h *Départ du centre*	*Après 8 h* *Départ du côté gauche*
Ta	6.8 cm	16.0 cm
Nb	9.8 cm	22.5 cm

Cependant, les expériences ci-dessus ont montré qu'en corrigeant les distances mesurées pour le courant d'électro-endosmose et de saturation la relation simple:

$$u_i = \frac{d_i \cdot \varkappa \cdot s}{i\, t} \cdot k\, k'$$

peut être appliquée — où k est un coefficient mesurant la longueur effective du papier par unité de longueur rectiligne, et k' un facteur tenant compte de la résistance par frottement, par adsorption, *etc.*

La valeur de k est donnée par la relation:

$$k = \frac{L'}{L} = \frac{R\, s\, \varkappa}{L}$$

où L' est la distance effective dans le papier et L la distance rectiligne — R est la résistance du ruban, $\varkappa$ la conductivité et s la section efficace[15].

Le facteur k' ne pourrait être déterminé que par comparaison. Négligeant ce facteur, la relation simple permet de comparer les mobilités relatives de différents ions de même signe. Nous avons calculé les valeurs u_i pour les ions complexes niobiques et tantaliques.

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Nous avons trouvé dans la solution tampon employée:

$$u_{Ta} : 0.89 \cdot 10^{-4} \text{ cm}^2/\text{V/sec}$$
$$u_{Nb} : 1.27 \cdot 10^{-4} \text{ cm}^2/\text{V/sec}$$

Ces résultats sont comparables aux vitesses trouvées dans la littérature pour d'autres ions complexes.

RÉSUMÉ

1. La séparation de Nb et de Ta à l'échelle micro a été étudiée par électrophorèse sur papier en employant des complexes oxaliques et citriques de Nb et de Ta et plusieurs mélanges tampons.

2. Une séparation satisfaisante est obtenue en employant des complexes oxaliques et comme solution tampon un mélange d'acide citrique et de citrate de potassium de pH 3.42 et de force ionique 0.4.

3. Les différents facteurs ayant une influence marquée sur le déplacement des ions par électrophorèse sur papier ont été étudiés et on a pu montrer qu'il est de première importance de supprimer les courants de saturation.

4. La suppression des courants de saturation est obtenue par conditionnement et en employant un montage à diaphragmes. Il s'est avéré que dans ces conditions le déplacement des ions dans le papier, sous ampérage et force ionique constants, est une fonction linéaire du temps d'électrophorèse, et des séparations difficiles deviennent possibles sur des rubans plus longs.

SUMMARY

A study has been made of the separation of Nb and Ta on a micro-scale by paper electrophoresis, using oxalic and citric complexes and different buffer solutions.

A fairly good separation is obtained by using oxalic complexes and, as buffer solution, a mixture of citric acid and potassium citrate of pH 3.42 and ionic strength 0.4.

Different factors influencing the displacement of ions by paper electrophoresis have been examined. It is shown that, if saturation currents are minimized, the displacement is practically proportional to the time of electrophoresis, and more difficult separations become possible using longer strips.

ZUSAMMENFASSUNG

Die Trennung von Nb und Ta in Form von Oxalat- und Zitratkomplexen wurde durch Papierelektrophorese und mit verschiedenen Pufferlösungen untersucht.

Eine gute Trennung wurde mit den Oxalatkomplexen und einer Pufferlösung von Zitronensäure und Kaliumzitrat von pH 3.42 und 0.4 Ionenstärke erhalten.

Zahlreiche Faktoren, welche die Bewegung der Ionen im Papier beeinflussen wurden untersucht. Es wurde gezeigt dass die Verschiebung proportional der Elektrophoresezeit ist wenn die Sättigungströme genügend herabgesetzt werden.

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A QUICK HETEROMETRIC MICRODETERMINATION OF CALCIUM AS SULFATE IN EXCESSES OF MAGNESIUM OR OTHER SUPPLEMENTS

by

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INTRODUCTION

Many methods for the determination of calcium are known. Our purpose was to investigate the necessary conditions for the application of these methods to a precise and quick heterometric determination of calcium. From our experience we know that no parallel can be drawn between micro- or macro-gravimetry and heterometry because different factors are of primary importance in the latter case. Therefore, experience with a given gravimetric method cannot be transferred automatically to heterometry[1-2]. Thus the advantages offered by the delicate oxalate method cannot be exploited in heterometry because of the different working conditions. The CaC_2O_4-precipitation occurs in heterometry at room temperature (at which we have worked so far), and no definite oxalate-hydrate is obtained.

In this report we present results for the determination of calcium as sulfate. The sensitivity of this determination is probably of the same order as with other anions such as phosphate, carbonate, *etc*. In addition, the determination of calcium as sulfate can be carried out in the presence of most other cations without the need for previous separation. No adjustment of pH is necessary and free acids, weak or strong, in excess, may be present in solution, if the other working conditions are maintained. If we disregard exceptional cases, a regular titration takes about 15 minutes. This length of time serves as an indication that the heterometric titration occurs normally. Titrations in the presence of large excesses of acids or salts, which interfere with the regular course of the reaction, take longer. 2-4 mg calcium are required for an analysis and the calcium may be determined with an error of 0.0-1.7%. It would be very difficult to take into consideration all the various conditions under which calcium solutions may be analysed. In this report we concentrate on the analysis of calcium in the presence of very large excesses of magnesium chloride. In the presence of other cations or anions only preliminary experiments have been carried out, but these were sufficient to show that no difficulties would be encountered in determining calcium in the presence of comparable quantities of other supplements. Neither divalent nor trivalent cations cause difficulties if present in amounts of the same order of magnitude as calcium, or in even greater amounts.

The method presented is especially useful for the determination of calcium in magnesium chloride solutions. Although calcium sulfate is insoluble in 90% ethyl alcohol, in pure calcium solutions the precipitation occurs with difficulty. For these analyses we used a Ca-solution which contained in 10 ml the maximum amount of calcium (4 mg); this gives a very low maximum optical density. We found that a minimum amount of $MgCl_2$ must be present. The optimum amount of $MgCl_2$ which is necessary, is approximately proportional to the amount of calcium in the analysed solution and is very high. The calcium therefore accounts for only a few percent of the total metal content. The heterometric method requires some experience and the advantage of the method becomes obvious if large numbers of such determinations have to be made. If calcium is present as phosphate or carbonate it has to be dissolved in a minimum of strong acid and then diluted with alcohol which already contains the necessary amount of magnesium chloride. The percentage of calcium in the concentrated magnesium chloride may be as low as 2-3%.

The influence of increased concentrations of magnesium chloride on the maximum density values, and on the character of the heterometric curves obtained, is very interesting and instructive and will therefore be more fully discussed later in this paper.

EXPERIMENTAL

Chemicals and solutions

Ordinary distilled ethyl alcohol of about 94% alcohol was used throughout this investigation. The reagents were all Baker, 'AnalaR' or c.p. Crystallized calcium chloride ($CaCl_2.6H_2O$) AnalaR was used. The magnesium chloride was $MgCl_2.6H_2O$ 'AnalaR'. The sulfuric acid was dissolved in alcohol and then brought to an alcohol content of 90% by volume. In all titrations of calcium with sulfuric acid, or *vice versa*, the molarity of both reagents was the same.

Apparatus and working conditions

All the titrations were carried out with a Heterometer. The technique and the working conditions were the same as in previous heterometric investigations[1]. The fundamentals of the heterometric method are presented in a separate paper[2].

The end-points of the titrations were obtained from enlarged titration curves in the following way: a line, which was generally horizontal, was drawn through a few points of the constant maximum densities. Another line was drawn through the measured points of the last part (= the last quarter) of the titration. The point of intersection of this line with the maximum density line was taken as the end-point (= X) of the titration.

RESULTS AND DISCUSSION

General: A selection of results is compiled in two tables whilst the curves of some experiments are presented in Fig. 1. The numeration is the same in the tables and the curves. From the results obtained the following may be deduced: the titrations of calcium chloride with sulfuric acid could not be carried out well in pure alcoholic calcium chloride solutions, although clear end-points were obtained (Table 1, expts. 1 and 9). The maximum densities obtained are very low even with the highest concentration of calcium used. The addition of acetic acid or sodium acetate does not improve the results (in the presence of acetate no precipitation occurred, expt. 2.). We soon ascertained that the addition of magnesium chloride acts favourably on the precipitate and that the maximum optical densities obtained in the presence

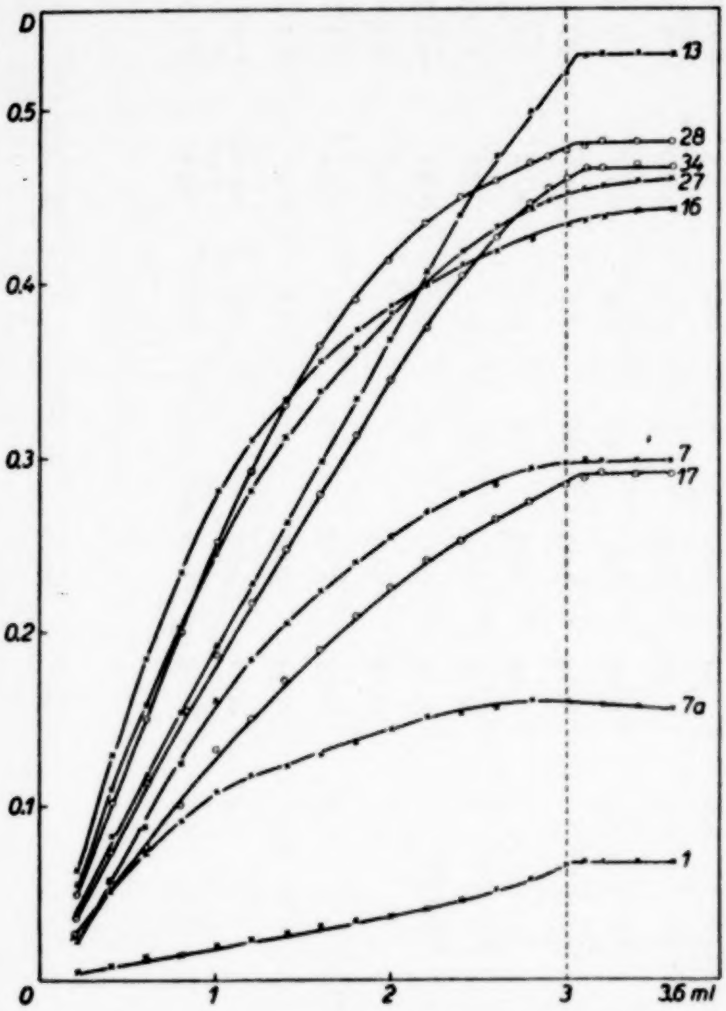

Fig. 1. Titration curves of calcium chloride with sulfuric acid.

of magnesium chloride are about three times higher, than in its absence. The effects which were obtained with various other supplements could not be studied with certainty, unless the solution contained a minimum amount of magnesium chloride, because the density values were low and no clear results were obtained. Therefore, these experiments with added supplements were carried out in the presence of an optimum amount of magnesium chloride. The addition of acetic acid in all these cases had no influence and the experiments were therefore carried out in its presence.

Many parallel experiments were made with 3 ml $CaCl_2$ 0.02*M* and 3 ml $CaCl_2$ 0.04*M*, for the following reason: the maximum densities obtained in this investigation are low even when using a higher amount of calcium. This in general does not prevent a precise determination of calcium. But on working with too small an amount of calcium, the danger exists, that in the presence of a supplement (*e.g.* trivalent cation) the precipitation may be cancelled altogether, whilst if titrated in the presence of a larger amount of calcium, the influence of the supplements may be insignificant. Thus if a comparison is made of the results obtained in the presence of acids (Table 2), we see that in the presence of a smaller amount of calcium, the titration time is lengthened (expts. 17 and 18). If the same acid is added in the presence of a larger amount of calcium, the maximum density values are not lowered at all (expts. 27 and 28).

INFLUENCE OF MAGNESIUM CHLORIDE

In the heterometric titrations, magnesium chloride, of all salts tried, produces the most favourable effect on the precipitation. This can be seen from the tables as well as from Fig. 1. Magnesium chloride is very soluble in alcohol and high concentrations of this salt may be prepared. No other chloride shows a similar effect. With both the lower and the higher amount of calcium used, we obtain an optimum effect on increasing the amount of magnesium chloride added, approximately until the molar ratio Ca: Mg = 1 : 30. On further increasing the concentration of magnesium chloride, the maximum density values obtained slowly decrease. Simulta-

TABLE I

Composition: 3 ml $CaCl_2$ a*M* alc. + b ml supplements alc.
+ (7-b) ml alc. + x ml H_2SO_4 a*M* alc.

Temp. 18° C. Ca content: 2.405 mg or 4.81 mg

Expt. number	*Supplements*	*% Ca*	*Molarity (a)*	*End-point x ml H_2SO_4*	*Titration time in min*	*Initial precip. at ml*	*Maximum density value*	*% error*
1	6.5 ml alc. + 0.5 ml H_2O		0.02	3.02	16	0.3	0.07	+0.6
2	6.5 ,, ,, + 0.5 ,, CH_3COONa 2*M* aq.		0.02	∞				
3	5.0 ,, ,, + 1 ,, $MgCl_2$ *M* alc. + 1 ml CH_3COOH *M* alc.		0.01	2.95	19	0.6	0.14	−1.7
4	5.5 ,, ,, + 0.5 ,, ,, *M* aq. + 1 ,, ,, ,, ,,		0.02	2.95	13	0.2	0.22	−1.7
5	5 ,, ,, + 1 ,, ,, 2*M* alc. + 1 ,, ,, ,, ,,		0.02	3.00	15	0.2	0.27	0.0
6	3.5 ,, ,, + 2 ,, ,, *M* ,, + 1 ,, ,, ,, ,, + 0.5 ml H_2O	4.8	0.02	3.02	15	0.2	0.23	+0.6
7	4.0 ,, ,, + 2 ,, ,, 2*M* ,, + 1 ,, ,, ,, ,,	2.4	0.02	2.95	27	0.2	0.29	−1.7
7a	2 ,, ,, + 4 ,, ,, 2*M* alc. + 1 ,, ,, ,, ,,	1.2	0.02	2.9	45	0.4	0.15	−3.3
8	6.5 ,, ,, + 0.5 ,, H_2O		0.04	3.03	16	0.2	0.16	+1.0
9	4.5 ,, ,, + 0.5 ,, ,, + 2 ,, ,, ,, ,,		0.04	3.05	12	0.2	0.16	+1.7
10	6.5 ,, ,, + 0.5 ,, $MgCl_2$ *M* aq.		0.04	3.04	12	0.2	0.39	+1.3
11	6.5 ,, ,, + 0.5 ,, ,, 2*M* ,,		0.04	2.95	22	0.2	0.42	−1.7
12	5.5 ,, ,, + 0.5 ,, ,, 2*M* ,, + 1 ,, ,, ,, ,,		0.04	3.03		0.2	0.47	+1.0
13	4 ,, ,, + 2 ,, ,, 2*M* alc. + 1 ,, ,, ,, ,,	4.8	0.04	3.05	14	0.2	0.53	+1.7
14	3 ,, ,, + 3 ,, ,, 2*M* ,, + 1 ,, ,, ,, ,,		0.04	3.05	23	0.2	0.47	+1.7
15	2 ,, ,, + 4 ,, ,, 2*M* ,, + 1 ,, ,, ,, ,,	2.4	0.04	3.02	27	0.2	0.51	+0.6
16	6 ,, ,, 2*M* ,, + 1 ,, ,, ,, ,,	1.6	0.04	3.05	31	0.2	0.43	+1.7

TABLE II

Composition: 3 ml $CaCl_2$ a*M* alc. + b ml supplements alc. + (7-b) ml alc. + x ml H_2SO_4 a*M* alc.

Temp. 18° C. Ca content: 2.405 or 4.81 mg

Expt. number	*Supplements*	*% supplement*	*Molarity (a)*	*End-point x ml H_2SO_4*	*Titration time in min*	*Initial precip. at ml*	*Maximum density value*	*% error.*
17	2 ml $MgCl_2$ *M* alc. + 1 ml CH_3COOH *M* alc. + 1 ml HCl *M* alc. + 3 ml alc.		0.02	3.02	40	0.2	0.29	+0.6
18	2 ,, ,, ,, ,, + 1 ,, ,, ,, ,, + 5 ,, ,, ,, ,, ,,		0.02		100	1.4	0.16	
19	2 ,, ,, ,, ,, + 1 ,, ,, ,, ,, + 0.5 ml $MnCl_2$ *M* alc. + 3.5 ml alc.	92	0.02	2.96	15	0.2	0.27	−1.3
20	2 ,, ,, ,, ,, + 1 ,, ,, ,, ,, + 0.5 ml $ZnCl_2$ *M* alc. + 3.5 ml alc.	93.2	0.02	2.96	14	0.2	0.26	−1.3
21	2 ,, ,, ,, ,, + 1 ,, ,, ,, ,, + 4 ml $NiCl_2$ 0.1 *M* alc.	90.7	0.02	2.93	14	0.2	0.25	−2.3
22	2 ,, ,, ,, ,, + 1 ,, ,, ,, ,, + 0.5 ml $Cd(NO_3)_2$ *M* alc. + 3.5 ml alc.	96	0.02	2.95	21	0.2	0.24	−1.7
23	2 ,, ,, ,, ,, + 1 ,, ,, ,, ,, + 0.2 ,, $CuCl_2$ *M* alc. + 3.8 ,, ,,	84.4	0.02	2.95	20	0.2	0.27	−1.7
24	2 ,, ,, ,, ,, + 1 ,, ,, ,, ,, + 0.2 ,, $FeCl_3$ *M* alc. + 3.8 ,, ,,	83	0.02	2.97	25	0.2	0.27	−1.0
25	2 ,, ,, ,, ,, + 1 ,, ,, ,, ,, + 0.2 ,, $Cr(NO_3)_3$ *M* alc. + 3.8 ,, ,,	81	0.02	2.7	22	0.2	0.25	
26	2 ,, ,, ,, ,, + 1 ,, ,, ,, ,, + 1 ,, $AlCl_3$ 0.1*M* alc. + 3 ,, ,,	53	0.02	2.95	15	0.2	0.25	−1.7
27	2 ,, ,, 2*M* ,, + 1 ,, ,, ,, ,, + 1 ml HCl *M* alc. + 3 ml alc.		0.04	3.1	10	0.2	0.46	+3.4
28	2 ,, ,, ,, ,, + 1 ,, ,, ,, ,, + 1 ,, HNO_3 *M* alc. + 3 ml alc.		0.04	3.02	8	0.2	0.48	+0.6
29	2 ,, ,, ,, ,, + 1 ,, ,, ,, ,, + 1 ,, H_3PO_4 0.2*M* alc. + 3 ml alc.		0.04	3.05	22	0.2	0.42	+1.7
30	2 ,, ,, ,, ,, + 1 ,, ,, ,, ,, + 0.2 ml H_3 Citrate *M* alc. + 3.8 ml alc.		0.04	3.04	17	0.2	0.50	+1.3
31	2 ,, ,, ,, ,, + 1 ,, ,, ,, ,, + 0.5 ,, $Al(NO_3)_3$ 0.5*M* alc. + 3.5 ml alc.	59.3	0.04	3.10	26	0.2	0.43	+3.3
32	2 ,, ,, ,, ,, + 1 ,, ,, ,, ,, + 0.5 ,, $Cr(NO_3)_3$ 0.5*M* alc. + 3.5 ml alc.	72	0.04	2.9	12	0.2	0.46	−3.3
33	2 ,, ,, ,, ,, + 1 ,, ,, ,, ,, + 0.2 ,, $FeCl_3$ 0.5*M* alc. + 3.8 ml alc.	56	0.04	3.0	18	0.2	0.45	0.0
34	2 ,, ,, ,, ,, + 1 ,, ,, ,, ,, + 0.5 ,, $FeCl_3$ 0.5 ,, ,, + 3.5 ,, ,,	74.5	0.04	2.96	12	0.2	0.47	−1.3

neously, the titration time gradually increases and the location of the first maximum optical density point becomes less certain. It is remarkable that the optimum effect when the higher amount of calcium is used lies at a higher concentration of magnesium chloride than is the case with the lower amount of calcium.

Analysing the results we may arrive at the following explanation of what happens in the ethyl alcoholic solutions. In the absence of magnesium chloride the titration time remains the same as in the presence of the optimum concentration of magnesium chloride, but the $CaSO_4$ particles formed absorb the light less and are probably smaller. The addition of magnesium chloride increases the growth of the solid particles although their number may be less than is the case in the absence of magnesium chloride. Magnesium nitrate apparently does not have a similar effect to magnesium chloride. The presence of NH_4Cl does not show a clear influence of the chlor anions. On the other hand, if it is caused by the binding of water molecules to magnesium chloride, then less magnesium chloride would be required at the optimum with the higher amount of calcium. But the opposite is the case. It must therefore be assumed that a distinct interrelation exists between the amount of calcium and the concentration of magnesium chloride at the optimum. If these results are compared with those obtained in the heterometric determination of calcium as calcium-phthalate[3], also in the presence of magnesium, we arrive at the following conclusions: the favourable influence of the lower concentrations of magnesium chloride on the heterometric precipitation of $CaSO_4$ is probably *specific* for this reaction. In addition there is a negative effect due to increasing viscosity with increasing concentration of magnesium chloride. In both reactions this has a retarding effect on the formation of the particles; this effect is of the same character both in the case of $CaSO_4$ and in that of Ca-phthalate.

INFLUENCE OF SUPPLEMENTS

The addition of supplementary salts or acids to a $CaCl_2$-solution, which contains approximately an optimum amount of magnesium chloride, causes no further improvement in the results obtained. Some results may be seen in Table II. Since these are preliminary experiments, they only permit us to draw general conclusions. The presence of bivalent cations in a molar concentration which is either equal or even higher than the molar concentration of calcium, has no measurable influence on the heterometric titration of calcium. There is a negative effect if trivalent cations as chlorides or nitrates are present in higher concentrations; the determination of the end-point becomes illusory even if the maximum density value does not decrease. But if the molar concentration of the supplementary salts is of the same order as that of the calcium chloride, the supplement does not interfere. The same occurs with phosphoric or citric acid which do not influence the results when present in moderate amounts.

DETERMINATION OF CALCIUM

Solutions: A $2M$ solution of $MgCl_2$ in alcohol is prepared by dissolving pure crystallized $MgCl_2.6H_2O$ in 95% alcohol. A $0.04M$ solution of sulfuric acid 'AnalaR' in alcohol is generally used for the titration of calcium. A normal acetic acid solution is prepared by dissolving the necessary amount of acid in alcohol.

Method: 10 ml of an alcoholic solution ($>$ 90%) is analysed. The solution contains: 2-4 mg calcium (as $CaCl_2$ or $Ca(NO_3)_2$) in addition to 1 ml N acetic acid and 2 ml 1-2M $MgCl_2$. The solution is titrated heterometrically with a 0.04M sulfuric acid. The end-point is obtained by the intersection of the maximum density line with the last part of the titration line. Titration time 15 minutes. Error 0-2%.

SUMMARY

An alcoholic solution of calcium chloride (2-4 mg Ca) which contains $>$ 95% magnesium as chloride besides other impurities can be titrated directly heterometrically with a standardized alcoholic sulfuric acid solution. The titration lasts about 15 minutes at room temperature. Error 0-2%.

RÉSUMÉ

Une solution alcoolique de chlorure de calcium (2-4 mg Ca), renfermant $>$ 95% de chlorure de magnésium, et d'autres impuretés, peut être titrée hétérométriquement, directement, au moyen d'une solution alcoolique d'acide sulfurique étalon. Le titrage dure environ 15 minutes, à la température ordinaire. Erreur 0-2%.

ZUSAMMENFASSUNG

Eine alkoholische Calciumchlorid-Lösung (2-4 mg Ca), welche abgesehen von Verunreinigungen, $>$ 95% an Magnesiumchlorid enthält, kann mit einer standardisierten alkoholischen Schwefelsäure titriert werden. Titrationsdauer bei Zimmertemperatur etwa 15 Minuten. Fehler 0-2%.

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REVUES DE LIVRES

New Methods in Analytical Chemistry by RONALD BELCHER AND CECIL WILSON, Chapman and Hall Ltd., London, 1955, 287 pp., 30 s.

C'est pour moi un vrai plaisir d'annoncer ce livre, écrit par deux auteurs si éminemment compétents. Comme on peut le lire dans la préface, il y a parmi les analystes une tendance de croire que tout ce qui est vraiment neuf dans le domaine de la chimie analytique doit nécessairement se rattacher aux méthodes dites physiques ou instrumentales. Les auteurs ont parfaitement réussi à nous montrer qu'également en fait de l'analyse gravimétrique et volumétrique il existe un grand nombre de nouveautés dignes de notre sérieuse attention. Successivement ils nous présentent une pléthore de réactifs nouveaux pour les dosages gravimétriques, minéraux aussi bien qu'organiques (127 pp.), des indicateurs modernes pour l'acidimétrie et pour les dosages oxidimétriques (42 pp.), des liquides moins connus pour les titrages (30 pp.), et enfin un nombre de dosages modernes gravimétriques et titrimétriques pour une sélection d'éléments. Cet ensemble constitue une collection extrêmement précieuse de données et de renseignements que jusqu'à présent on n'eût pu se procurer qu'en étudiant une littérature très vaste et en outre éparpillée. Il nous convient d'être reconnaissants aux auteurs qui se sont donné tant de peine pour nous les présenter sous une forme condensée et synthétique, et par-dessus le marché si agréablement lisible. Ajoutons qu'après chaque chapitre une liste de références nous met à même de trouver les publications originales.

Que les auteurs me permettent d'exprimer le voeu que dans une deuxième édition — qui ne doit pas se faire attendre longtemps — ils prendront un peu plus d'intérêt aux travaux non-anglosaxons. L'importance de ce livre ne se limite pas aux anglais et aux américains; il est un excellent guide pour tous les analystes du monde entier.

C. J. VAN NIEUWENBURG (Delft)

Kolorimetrie-Photometrie und Spektrometrie, eine Anleitung zur Ausführung von Absorptions-, Emissions-, Fluorescenz-, Streuungs-, Trübungs- und Reflexionsmessungen von GUSTAV KORTUM, 3. neubearbeitete Auflage, Springer-Verlag, Berlin, 1955, 458 Seiten mit 186 Abbildungen, Ladenpreis: Ganzleinen DM 36.—.

Cette nouvelle édition a été remaniée et développée avec le soin et la minutie qui ont déjà fait le succès des autres livres du Professeur Kortüm. Le chapitre introductif traite des bases fondamentales de la spectrophotométrie, du domaine d'emploi et de la précision de ces méthodes, des erreurs systématiques.

L'étude des sources de lumières, celles des cuves de l'optique, des filtres, des stabilisateurs de tension et de divers accessoires font l'objet du chapitre suivant.

Viennent ensuite les méthodes visuelles et les méthodes électriques et photographiques. Sous le nom de méthodes thermoélectriques, l'auteur étudie la spectrophotométrie infrarouge.

L'analyste trouvera dans ce livre, non seulement une documentation approfondie sur les divers appareils en usage, sur les possibilités de chacun d'eux, la précision qu'on peut en attendre, mais aussi des considérations théoriques rigoureuses sur toute la colorimétrie, la photométrie et la spectrométrie. Outre la partie purement analytique, l'auteur montre comment il est possible de déterminer la constitution des molécules au moyen des ondes électromagnétiques.

Excellent ouvrage, fort bien présenté et très complet. Précieux instrument entre les mains de ceux qui s'intéressent aux méthodes optiques et à leurs applications.

D. MONNIER (Genève)

THE APPLICATION OF THIOSALTS IN ANALYSIS
IV. A NEW SCHEME OF QUALITATIVE ANALYSIS

Part B. INSOLUBLE SUBSTANCES IN QUALITATIVE ANALYSIS

by

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In a previous paper[1] a new scheme was put forward for the qualitative analysis of mixtures containing common elements, based on the formation and subsequent decomposition of the thiosalts. It was also shown that certain compounds are likely to be left as an "insoluble" residue after the mixture is subjected to standard acid treatment as outlined in *Procedure I* of this paper.

In a publication[2] from the University of Allahabad, a new scheme was proposed for the analysis of "insoluble substances" containing the compounds of the common as well as rare elements, with a brief review of the relevant properties of these compounds.

In this paper the author intends to give a mere outline of the procedure to be followed in case an insoluble residue is obtained after subjecting the mixture (containing only common elements) to standard acid treatment.

The insoluble residue may contain

Sulphates: $BaSO_4$, $SrSO_4$, $Cr_2(SO_4)_3$ (anhydrous), $PbSO_4$

Halides: AgCl, $CrCl_3$ (violet), CaF_2 (fluorspar)

Ignited Oxides: Al_2O_3, Cr_2O_3, SnO_2, Sb_2O_4, SiO_2

Complex ferro- and ferricyanides: Prussian Blue, Turnbull's blue, and cupric ferro- and ferricyanides

Stannic phosphate.

The following steps may be taken to identify systematically the compounds present in the insoluble residue:

Procedure I

Extract the residue with saturated ammonium acetate, $PbSO_4$ dissolves completely. Test the filtrate for lead with potassium chromate. A yellow precipitate shows the presence of lead sulphate.

Procedure II

Boil the insoluble residue from *Procedure I* with $4N$ sodium hydroxide solution and filter. Concentrate the filtrate to a small volume, evaporate to dryness with *aqua regia* to dehydrate silica and decompose the ferro- and ferricyanides. Take up the residue with $2N$ hydrochloric acid, filter and analyse as follows:

Ppt. 2 SiO_2,H_2O.	Filt. Chlorides of Al, Cr, Fe and Sb. Treat with 1*N* Na_2S in excess and filter.	
Test for silica by SiF_4 test in a lead or platinum dish.	Ppt. $Al(OH)_3$, $Cr(OH)_3$, Fe_2S_3. Test as usual.	Filt. Thiosalt of Sb. Acidify with dil. HCl. Boil and filter. An orange ppt. Shows **Sb**

The precipitate obtained after boiling with 4*N* sodium hydroxide solution is extracted with dilute hydrochloric acid and the solution containing the chlorides of Fe, Cr and Cu analysed as follows:

Add 1*N* Na_2S in excess and filter. Treat the precipitate of hydroxides and sulphides with dilute hydrochloric acid and filter.

Ppt. CuS (black). Test as usual.	Filt. Chlorides of Fe and Cr. Test as usual.

Procedure III

Treat the residue left after extraction with dilute hydrochloric acid in *Procedure II* with dilute ammonium hydroxide and test the filtrate for silver. If silver is found in the ammoniacal solution, test for the following acids which may have been decomposed by *aqua regia* with the formation of AgCl.

(a) Treat a portion of the original mixture with zinc and dilute sulphuric acid and test for chloride, bromide, iodide, cyanide and thiocyanate as usual.

(b) Test for ferro- and ferricyanides in the sodium carbonate extract of the original mixture for the detection of the acid radicals even in case silver is absent, as these acids are likely to be present due to other insoluble complex ferro- and ferricyanides.

Procedure IV

Fuse the residue with NaOH, Na_2CO_3 and KNO_3 (if coloured) in sufficiently large excess. The changes which will be brought about may be represented conveniently as follows:

$BaSO_4$	$SrSO_4$	CaF_2	$Cr_2(SO_4)_3$	Cr_2O_3	SnO_2	Sb_2O_4
↓	↓	↓	↓	↓	↓	↓
$BaCO_3$	$SrCO_3$	$CaCO_3$				
+	+	+				
Na_2SO_4	Na_2SO_4	NaF	Na_2CrO_4	Na_2CrO_4	Na_2SnO_3	Na_3SbO_4
			+			
$NaAlO_2$	Na_2SiO_3		Na_2SO_4	(Na_2SnO_3 + Na_3PO_4		
↑	↑			↑		
Al_2O_3	SiO_2			$Sn_3(PO_4)_4$		

(a) Crush and boil the fused mass with water. All the sodium compounds between the two lines will pass into solution. Filter and test the filtrate for

(i) Sulphate, phosphate, fluoride and silicate

(ii) Al, Cr, Sb and Sn.

(b) Boil the residue not dissolved by water in dilute acetic acid, filter and test the filtrate for Ba, Sr and Ca as usual.

Procedure V

SnS_2 (mosaic gold) and HgS (black) will undoubtedly go completely into solution on treatment with standard acids in *Procedure I*, but test for the sulphide radical in the residue left after boiling the original mixture with a saturated solution of sodium carbonate, with zinc and hydrochloric acid. These will be decomposed to give hydrogen sulphide.

References p. 99

SUMMARY

A scheme has been proposed for the systematic detection of compounds in the insoluble residue obtained in qualitative analysis of the common elements.

RÉSUMÉ

L'auteur propose un schéma de détection systématique des composés pouvant se trouver dans les résidus insolubles, obtenus lors de l'analyse qualitative des éléments courants.

ZUSAMMENFASSUNG

Der Autor schlägt ein Schema vor zur systematischen Auffindung der Verbindungen, welche sich in unlöslichen Rückständen befinden können, die man während der qualitativen Analyse der gebräuchlichen Elemente erhalten hat.

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IDENTIFICATION SPÉCIFIQUE DES ACIDES AMINÉS ET DES VITAMINES PAR L'INDICE DE RÉFRACTION ET LA TEMPÉRATURE EUTECTIQUE

APPLICATION A LA CHROMATOGRAPHIE SUR PAPIER ET AU CONTRÔLE

par

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Les deux classes de composés envisagés ici ne bénéficient pas des moyens d'identification courants (température de fusion, des individus ou de leurs dérivés) des corps organiques[1]. D'autre part, leur identification par la solubilité, le pouvoir rotatoire, la densité, présente soit des lacunes, soit un manque de conditions standard. Le R_F en chromatographie est actuellement le moyen d'identification le plus sûr, mais demande à être contrôlé[2]. L'identification de ces substances doit d'autre part tenir compte de leur fragilité aux réactifs et à la chaleur, aussi dans certains cas, de leur prix élevé. C'est pourquoi, nous avons envisagé pour cette contribution un moyen réalisable sur aussi peu de substance que possible (quelques microgrammes) par des techniques susceptibles de ne pas démolir les individus.

L'indice de réfraction semble à ce point de vue préférable: quelques microgrammes suffisent à sa détermination par immersion à la température ordinaire et la précision à laquelle on peut prétendre est de 0.002 unités, si l'on travaille en lumière monochromatique et à température constante. Cette constante a l'avantage de pouvoir se mesurer sur un cristal faisant partie d'un mélange. Par conséquent, elle est susceptible d'être utile pour l'analyse de taches chromatographiques (après élution et évaporation du solvant ou après sublimation). L'observation des lignes de Becke dans des liquides de référence (dont l'indice est connu à la 4ème décimale près), sous le microscope polarisant, a été décrite ainsi que la manière de procéder pour déterminer les indices conventionnels n_p et n_g des individus, sans procéder à des coupes orientées[3].

Nous donnons les renseignements à ce sujet concernant 38 acides aminés et 14 vitamines. Ces renseignements peuvent, sans aucun doute, servir dans le contrôle proposé et surtout dans le contrôle de pureté des individus. Mais il apparaît que la spécificité de cette constante n'existe que pour 50% des cas d'acides aminés examinés et que dès lors il est impossible de s'en tenir uniquement à cette détermination pour identification. Il a été prouvé que l'origine des acides aminés et des vitamines ne joue aucun rôle dans la valeur de l'indice[3].

D'autre part, d'intéressants effets de structure sur la grandeur de l'indice sont perceptibles et ont été notés au cours de ce travail.

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* Dir.: A. LACOURT.

Ont une action:

— la position des fonctions NH_2 et COOH (*β*- et *α*-alanine et acide *ε*-aminocaproïque)

— l'allongement de la chaîne (DL-*α*-alanine, L-*α*-alanine, acide DL-*α*-aminobutyrique, DL-norvaline, DL-norleucine, L-norleucine)

— la ramification de chaîne (*iso*propylique: DL-norvaline, DL-valine, L-valine, DL-norleucine, DL-leucine, L-leucine; *iso*butylique: DL-norvaline, DL-leucine, DL-*iso*leucine)

— la substitution d'un CH_3 par COOH, C_6H_5, C_6H_4OH, CH_2OH, CH_2SH et le remplacement d'un CH_2OH par un CH_2SH.

TABLEAU I

INDICES DE RÉFRACTION DES ACIDES AMINÉS (MÉTHODE PAR IMMERSION, ±0.002)*

Acides expérimentés	n_p *à 20°*	n_g *à 20°*	*Poids moléculaire*	*Densité*
Glycine	1.619	1.657	75.07	1.601 1.607
β-Alanine	1.524	1.583	89.09	1.404
Ac. *ε*-Aminocaproïque	1.504	1.536	131.17	—
DL-*α*-Alanine	1.539	1.579	89.09	1.424
L *α*-Alanine	1.517	1.560	89.09	1.401
Ac. DL-*α*-Aminobutyrique	1.517	1.543	103.12	1.231
DL-Valine	1.580	1.602	117.15	1.316
L-Valine	1.553	1.585	117.15	1.230
DL-Norvaline	1.481	1.502	117.15	—
DL-Leucine	1.538	1.558	131.17	1.191
L-Leucine	1.525	1.543	131.17	1.165
DL-*Iso*leucine	1.552	1.581	131.17	—
L-*Iso*leucine	1.536	1.560	131.17	—
DL-Norleucine	1.522	1.558	131.17	1.169
L-Norleucine	1.524	1.554	131.17	—
Ac. DL-Aspartique	1.524	1.628	133.10	1.663
Ac. L-Aspartique	1.504	1.620	133.10	—
Ac. DL-Glutamique	1.526	1.539	147.13	1.460
Ac. L-Glutamique	1.504	1.619	147.13	1.538
DL-*β*-Phénylalanine	1.619	1.657	165.19	—
L-*β*-Phénylalanine	1.607	1.660	165.19	—
DL-Tyrosine	1.560	1.658	181.18	—
L-Tyrosine	1.525	1.640	181.18	1.456
L-Arginine.HCl	1.572	1.595	174.21 + HCl	—
L-Histidine.HCl	1.593	1.620	155.16 + HCl	—
L-Histidine	1.525	1.619	155.16	—
DL-Lysine.2HCl	1.545	1.568	146.19 + 2HCl	—
L-Lysine.2HCl	1.560	1.569	146.19 + 2HCl	—
DL-Tryptophane	1.607	1.658	204.22	—
DL-Thréonine	1.525	1.597	119.10	—
L-Thréonine	1.526	1.593	119.10	—
DL-Méthionine	1.568	1.604	149.21	1.340
L-Méthionine	1.560	1.584	149.21	—
DL-Sérine	1.558	1.578	105.90	1.537
L-Cystéine	1.608	1.622	121.15	—
L-Proline	1.552	1.576	115.13	—
Créatine	1.528	1.586	131.14	—
Créatinine	1.620	1.742	113.12	—

* La température d'observation a été 20° ± 0.1° dans l'éclairage au sodium.

Dans tous les cas des acides aminés, le passage d'un isomère DL à un isomère L est marqué par une diminution de la valeur du plus petit des indices, n_p (voir Tableau I).

Tous les acides aminés sont solubles dans l'eau et l'évaporation de leur solution à la température ordinaire améliore souvent l'aspect des cristaux destinés aux déterminations d'indices. Il ne faut pas qu'ils soient trop épais. Dans ce cas, mieux vaut les recristalliser que les broyer. La sublimation permet aussi d'obtenir des cristaux convenables; tous les acides examinés — sauf le DL-aspartique et l'arginine — subliment à température plus basse que la fusion[4].

Avec les vitamines (voir Tableau II), nous n'avons jamais procédé autrement que par cristallisation préalable à la détermination des indices. Au départ, tous les acides aminés ont été examinés au point de vue de leur pureté (constance de l'indice, stabilité d'eutectique après cristallisation).

TABLEAU II

INDICES DE RÉFRACTION DES VITAMINES (MÉTHODE PAR IMMERSION, ± 0.002)*

Vitamines	*T° Fus.*	n_p *à 20°*	n_g *à 20°*	*Indice à la fusion (méthodes des poudres)*[4]
Nicotinamide	129/131	1.477	1.742	1.5502 à 130° 1.5403 à 156°
Ac. Nicotinique	234/237	1.481	1.742	1.4936 de 240° à 241°
Ac. *Iso*nicotinique	137	1.445	1.742	
Ac. *o*-Aminobenzoïque	145	1.504	1.746	1.5700 de 145° à 147° 1.5611 de 165° à 168°
Ac. *m*-Aminobenzoïque	174/179	1.530	1.742	1.5611 de 175° à 178°
Ac. *p*-Aminobenzoïque	187	1.530	1.742	1.5795 à 193°
Pyridoxine . 2HCl	160 déc.	1.553	1.697	
Pyridoxal . 1HCl	207/214	1.560	1.623	1.5897 à 207°
Adermine (Vit.B6)				1.6011 ,,
Aneurine (Vit. B_1)	245/250	1.598	1.700	
Hespéridine (Vit. P)	251/254	1.553	1.685	
Vitamine B_2	282 déc.	1.658	1.658	
Ac. Folique	infus. 250 déc.	1.560	1.742	
Ac. L-Ascorbique	190/192	1.481	1.694	1.5101 à 195° 1.5204 ,,
Ac. D-*Iso*ascorbique		1.536	1.688	

* Observations à 20° ± 0.1° en éclairage au sodium.

L'étude systématique *des eutectiques binaires* a révélé pour les acides aminés des résultats beaucoup plus spécifiques, permettant le plus souvent de distinguer les isomères les uns des autres.

La technique employée pour la préparation des mélanges ne peut faire usage de la méthode de contact, à cause de la fragilité des substances étudiées. On procède par simple broyage des individus entre deux porte-objets ou par mise en solution. Il s'agit de voir la première fusion dans ce mélange chauffé sous le microscope polarisant[3]. 18 acides et 9 vitamines ont été examinés ainsi.

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Les effets de structure se sont encore révélés beaucoup plus déterminants des eutectiques que la proximité des points de fusion des partenaires ou que leur système cristallin.

Bon nombre d'eutectiques liquides à la température ordinaire n'ont pas encore été étudiés, mais mériteraient de l'être. Ils sont néanmoins caractéristiques déjà. Un bon nombre de ces eutectiques sont fusibles en-dessous de 100° et ne risquent donc pas d'altérer les acides aminés chauffés. L'identification par les eutectiques seuls n'est pas possible. Elle l'est davantage si on la combine avec la détermination de l'indice de réfraction. Les acides aminés forment des eutectiques entre eux et aussi avec un grand nombre de partenaires. Les tableaux qui suivent montrent l'usage que l'on peut faire de ces deux propriétés pour aboutir à l'identification des individus et préciser auquel des isomères on a affaire. Le choix des eutectiques est très grand pour ne pas être gêné dans ses conclusions, même dans les cas les moins favorables.

Le groupe important des *leucine, isoleucine* et *norleucine*, par exemple, qui migrent souvent en une seule tache[5] sont reconnaissables par des indices différents dans le mélange sublimé du papier.

D'autre part, les individus isolés ont des températures de fusion eutectique nettement différentes avec plusieurs partenaires. Pour des acides comme la *glycine* et la *β-phénylalanine* difficiles à reconnaître par leurs températures de fusion et par leurs indices de réfraction, la température de fusion eutectique de mélanges binaires permet de décider auquel des deux l'on a affaire (voir Tableaux III, IV A et IV C).

TABLEAU III

GLYCINE ET DL-β-PHENYL ALANINE

	Glycine *T°Fus. 240/247*	*DL-β-Phénylalanine* *T°Fus. 225/240 déc.*
Indices de réfraction		
n_p à 20°	1.619	1.619
n_g à 20°	1.657	1.657
Partenaire	*Fusion des eutectiques binaires*	
Ac. Malonique	liquide	105
Ac. Succinique	144	158/159
Ac. Tartrique	liquide	130
Ac. Ascorbique	130/131	159/160
Ac. Hippurique	175/176	160

Pour le groupe des *acides aspartiques* et *glutamiques* dont la séparation chromatographique est assez rare, on est aidé dans l'analyse de telles taches globales par le fait que l'acide aspartique ne sublime pas tandis que les glutamiques subliment. Le tableau des identifications spécifiques montre le parti que l'on peut tirer des deux propriétés qui ont été étudiées ici, en vue de l'identification des acides aspartiques, DL-et L-glutamiques (voir Tableau IV B).

TABLEAU IV

IDENTIFICATION SPÉCIFIQUE DES ACIDES AMINÉS

A. GLYCINE, ACIDE ε-AMINOCAPROIQUE, DL-α-, L-α- ET β-ALANINE

Propriétés physiques		*Glycine*	*β-Alanine*	*ε-Amino caproïque*	*DL-α-Alanine*	*L-α-Alanine*
Température de fusion		240/247	202/205	205/210	257 déc.	266 déc.
Densité		1.601 1.607	1.404		1.424	1.401
Indice de réfraction (20°, Na)						
n_p		1.619	1.524	1.504	1.539	1.517
n_g		1.657	1.583	1.536	1.579	1.560
Partenaire	*T° Fus. parten.*	*Température de fusion des eutectiques binaires*				
Glycine	240/247		166/168	193/195	négat.	négat.
β-Alanine	202/205	166/168	—	169	négat.	négat.
ε-Aminocaproïque	205/210	193/195	169	—	192/194	180/182
DL-α-Alanine	257 déc.	négat.	négat.	192/194	—	négat.
L-α-Alanine	266 déc.	négat.	négat.	180/182	négat.	—
DL-α-Aminobutyrique	200	négat.	négat.	174/177	négat.	négat.
DL-Aspartique	> 310	202/203	155/156	145/148	217	214
DL-Glutamique	180/183	172/174	158/160	144/146	165	165/166
L-Glutamique	194/198	185/187	163/164	154/156	189	176/177
Ac.Oxalique (subl.)	189	131/132	108	102	146/147	163
Ac.Malonique	131/136	liq.	liq.	liq.	liq.	liq.
Ac.Succinique	188	144/145		97	151/152	150/152
Ac.Adipique	154	146	90/92	69	146/147	140/142
Ac.Tartrique	169	liq.	liq.	78/78.5	liq.	liq.
Ac.Ascorbique	186	130/131	101/104	92	139/141	141
Glucose	146	140 déc.	141 déc.	115 déc.	137/139	135/136
Lactose	201	déc.	déc.	133/134	164/166	162/164
Mannitol	167	156		147/148	159	161/162
Ac.*o*-Hydroxybenzoïque	157	négat.	liq.	liq.	148/149	138
Ac.*p*-Hydroxybenzoïque	214	négat.	115/117	131	172/173	181/182
Nipagine M	127.5	119/120	123	112/113	118/119	124/126
Aspirine	133/144	126/127	95/97	69/71	123	124
Hydroquinone	172	négat.	112/114	140	163/165	161/162
Résorcine	110.5	104/106	liq.		103	96
Pyrogallol	133	105/106	,,	71/74	102	109/110
Ac. Hippurique	190	174/176	118/120	128	153/154	164/166
α-Chloracétamide	119.5	115/116	83/86	96/100	113	117/118
Saccharine	228	170/171	liq.	liq.	166/167	165/166
Urée (subl.)	135	125/126	112	115/116	126	124
Dicyandiamide	210	179/180	151/153	154/155	175/176	175/177
Thiourée	178/179	163/164	132/135	134/135	164/166	159/163

B. ACIDES DL-ASPARTIQUE ET DL- ET L-GLUTAMIQUES

Propriétés physiques	*Ac.DL-Aspartique*	*Ac.DL-Glutamique*	*Ac.L-Glutamique*
Température de fusion	> 310	180/183	194/198
Densité	1.663	1.460	1.538
Indice de réfraction (20°, Na) n_p	1.524	1.526	1.504
Indice de réfraction (20°, Na) n_g	1.628	1.539	1.619

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TABLEAU IVB (SUITE)

Partenaire	*T° Fus. parten.*	*Température de fusion des eutectiques binaires*		
		Ac. DL-*Aspartique*	*Ac.*DL *-Glutamique*	*Ac.* L-*Glutamique*
Glycine	240/247	202/203	172/174	185/187
β-Alanine	202/205	155/156	168/160	163/164
ε-Aminocaproïque	205/210	145/148	144/146	153/156
DL-α-Alanine	257 déc.	217	165	189
L-α-Alanine	266 déc.	214	165/166	176/177
DL-α-Aminobutyrique	200	179/182	159/162	176/178
DL-Norvaline	275 déc.	235/237	174/176	186
DL-Norleucine	250 déc.	242/243	173/175	187/188
DL-Aspartique	$>$ 310		172/173	187/189
DL-Glutamique	180/183	172/173		173
L-Glutamique	194/198	187/189	173	
L-Arginine. HCl	208/220			188/191
L-Histidine. HCl	250 déc.			191/192
DL-Tryptophane	250 déc.			191
L-Tryptophane	250 déc.			négat.
DL-Thréonine	233/235			185/187
DL-Méthionine	235 déc.			188/190
L-Cystéine	225 déc.			189/192
L-Cystine	220 déc.			187/190
L-Proline	222			159/164
Créatine	250/252			180/184
Créatinine	240 déc.			184/186
Ac. Oxalique (subl.)	189	45/46	50/52	64/65
Ac. Malonique	131/136	99/102	60/63	101
Ac. Succinique	188	177/180	156/158	170/171
Ac. Tartrique	169	141/143	95/98	135
Ac. Ascorbique	186	170/171	148/150	165/166
Ac.*p*.-Hydroxybenzoïque	214	négat.	172/173	182/184
Aspirine	135	négat.	125 subl.	122
Ac. Hippurique	190	négat.	165/166	174/175
Saccharine	228	218/219	174/175	185/187
Dicyandiamide	210	168/170	150/152	166/167
Thiourée	178/179	négat.	156/158	169/170

C. DL-β PHÉNYLALANINE, DL-LEUCINE, DL ISOLEUCINE ET NORLEUCINE

Propriétés physiques		DL-β-*Phénylalanine*	DL-*Leucine*	DL-*Isoleucine*	DL-*Norleucine*
Température de fusion		225/240	242/252	235	250 déc.
Densité			1.191		1.170
Indice de réfraction (20°, Na) n_p		1.619	1.538	1.552	1.522
Indice de réfraction (20°, Na) n_g		1.657	1.558	1.581	1.558
Partenaire	*T° Fus. parten.*	*Température de fusion des eutectiques binaires*			
Ac. Oxalique (subl.)	189	129	150/151		127
Ac. Malonique	131/136		liq.	68/70	83
Ac. Adipique	154		139/142	143	146/147
Ac. o-Hydroxybenzoïque	154/157	138/140	145/146	140	141/144
Ac. p-Hydroxybenzoïque	214	197	205	négat.	189
Ac. Hippurique	190	160	173/174	168/169	170
Ac. Diiodohippurique	209/218		203/204	190	197/200
α-Chloracétamide	119.5		109/110	± 100	négat.
Saccharine	228	172/176	187/188	171/172	186
Dicyandiamide	210		192	189/190	183/188
2.4.D.N.Phénylhydrazine	195/202		185/187	184	175/179
ε-Aminocaproïque	205/210	186	201/203	193/195	188
Ac. DL-Aspartique	$>$ 310	négat.	négat.	négat.	242/243
Ac. DL-Glutamique	180/183	négat.	négat.	négat.	173/175
Ac. L-Glutamique	194/198	négat.	négat.	négat.	187/188

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TABLEAU V

EUTECTIQUES BINAIRES DES VITAMINES

Vitamines	*T° Fus. vitamines*	*Partenaires*	*T° Fus. partenaires*	*T° Fus. eutectiques (loc.cit. 5)*
Nicotinamide	129/131	Acétanilide	115	89
		Phénacétine	135	106
Ac.Nicotinique	234/237	Salophène	190	180
		Dicyandiamide	210/212	150
Ac.*o*-Aminobenzoïque	145	Phénacétine	135	98
		Benzanilide	163	122
Ac.*m*-Aminobenzoïque	174/179	Benzanilide	163	141
		Salophène	190	152
Ac.*p*-Aminobenzoïque	187/(193)	Benzanilide	163	140
		Salophène	190	183
Adermine (vit. B_6)	207/214	Salophène	190	183
		Dicyandiamide	210/212	151
Aneurine (vit. B_1)	245/250	Salophène	190	184
	232/237	Dicyandiamide	210/212	142
Riboflavine (vit. B_2)	282 déc.	Salophène	190	189
		Dicyandiamide	210/212	191
		Phénolphtaléine	263	248
Ac. L-Ascorbique	190/192	Benzanilide	163	159
		Salophène	190	174

ANALYSE D'UNE TACHE SUR PAPIER FILTRE

Un papier filtre porteur d'un produit organique peut facilement en être débarrassé par élution; après évaporation du solvant, le résidu est alors identifié. Si la substance organique est un acide aminé, il est plus facile et plus rapide de découper une fraction du papier chargé et de le soumettre à la sublimation en chambre humide, à basse température, que d'en faire une élution.

Le papier et l'acide aminé présumé sont déposés humectés, sur un porte-objet reposant sur le bloc chauffant[5] à une température comprise entre 100° et 200°. Le R_F de la tache fait présumer la présence d'un acide donné et d'après cela, la température à laquelle se poursuivra la sublimation sera fixée. Un anneau de cuivre chauffé est ensuite placé autour de la tache et du papier, puis sur l'ensemble, est retourné un porte-objet chauffé, portant une goutte d'eau vers l'intérieur de la chambre. Au-dessus, à l'extérieur, se place un bloc de cuivre chauffé qui maintient tout au long de la sublimation une température favorable à la cristallisation des produits sublimés.

Après sublimation, le sublimat est mis dans une enceinte desséchante, avant de procéder aux déterminations d'indice ou d'eutectique. Lorsqu'il entre dans les intentions d'identifier par eutectique, la goutte d'eau placée au-dessus du papier contient en outre le cristal du partenaire eutectique choisi. Au cours de la sublimation, l'eutectique se forme — si eutectique il y a — à la surface du cristal du partenaire et on obtient ainsi une sorte de préparation de contact, très bien constituée. Il suffit alors après dessiccation, de gratter la préparation et d'observer la première fusion qui est toujours très facile à observer.

On obtient en une nuit, à 120°, une bonne sublimation d'acide glutamique. Les expériences faites à l'aide d'acide DL- et L- glutamique, et ensuite à l'aide de mélanges avec le DL- aspartique sont absolument démonstratrices. La température de fusion des eutectiques obtenus est bien la même que celle que l'on a observée avec les individus à l'état pur.

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TABLEAU VI

IDENTIFICATION DES ACIDES GLUTAMIQUES APRÈS SUBLIMATION

(Analyse d'une tache chromatographique sur papier)

Acides aminés contenus dans la tache sur le papier (µg)	*Partenaire eutectique µg*	*Sublimation*		*T° Fusion eutectique binaire*	
		T°	*Durée*	*observée*	*théorique*
Ac.DL-Glutamique (120 µg)	Ac.Oxalique (subl.) (120 µg)	120°	7 h	53/55/52 50/54 M/5 = 52° 8	50/52
id.	Dicyandiamide (120 µg)	120°	15 h	154/150 153/152 151/154 M/6 = 152° 3	150/152
id.	Ac. Oxalique (subl.) (120 µg)	120°	7 h	62/63/65 65/60/62 63/65/67 68 M/10 = 64°	64/65
id.	Dicyandiamide (120 µg)	120°	17 h	167/169 166/168 167 M/5 = 167° 4	166/167
Ac.DL-Glutamique (120 µg) Ac.DL-Aspartique (120 µg)	Dicyandiamide (30 µg)	120°	17 h	153/150 151/151 152/153 151/150 150/153 152 M/11 = 151° 4	150/152
Ac.DL-Glutamique (360 µg) Ac.DL-Aspartique (120 µg)	Dicyandiamide (30 µg)	120°	17 h	154/151 152/152 154/152 151/154 M/8 = 152°	150/152
Ac.DL-Glutamique (480 µg) Ac.DL-Aspartique (120 µg)	Dicyandiamide (30 µg)	120°	17 h	153/152 154/150 151/152 152/155 152/155 155/154 M/10 = 152° 8	150/152
Ac.L-Glutamique (120 µg) Ac.DL-Aspartique (120 µg)	Dicyandiamide (30 µg)	120°	19 h	165/167 167/164 166 M/5 = 166°	166/167

La dicyandiamide est préférable pour identifier de cette manière les acides glutamiques, parce qu'elle ne donne pas lieu à des phénomènes d'hydratation comme l'acide oxalique.

Cette même technique simple peut être étendue au contrôle de taches d'acides aminés simples, puisque tous subliment. Pour des taches globales, il serait nécessaire de développer l'étude des eutectiques ternaires. On peut compléter par la mesure de l'indice de réfraction pour reconnaître ces individus sublimés dans le mélange. Ceci

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s'appliquerait à l'analyse d'une tache chromatographique globale de phénylalanine, de leucine, d'*iso*leucine, et de norleucine.

Et comme indices et eutectiques sont affectés par l'isomérie (DL, L ou D) ces expériences peuvent renseigner sur la nature de l'isomère dans le mélange, renseignement que ne fournit pas le R_F.

CONCLUSION

La technique qui est préconisée ici pour l'analyse des taches d'acides aminés chromatographiés sur papier est basée sur la détermination des indices de réfraction et sur la température de fusion des eutectiques binaires. Les données qui servent de base à cette technique peuvent également servir au contrôle de pureté des individus isolés.

Elles permettent en effet de se rendre compte de la pureté isomérique, ce que ne fait pas la chromatographie.

Etant donné l'importance des acides aminés et des vitamines, il serait utile de poursuivre ces recherches.

Les indices de réfraction sont obtenus à ± 0.002 unités près et les fusions eutectiques à ± 1 à 2° près. La présence d'impureté peut être repérée selon le cas à partir de 1 à 3%. Tout dépend de l'allure des diagrammes thermiques des individus caractérisés avec leurs partenaires eutectiques.

RÉSUMÉ

L'indice de réfraction et la température de fusion eutectique de mélanges binaires, sont deux propriétés qui permettent une identification spécifique des individus et des isomères organiques. Elles ont été expérimentées à cet effet sur un certain nombre de vitamines et d'acides aminés. Il en résulte que l'analyse d'une tache globale d'acides aminés, sur papier devient facile grâce à ces propriétés. Un exemple relatif aux acides glutamiques, montre que cette analyse renseigne mieux que le R_F chromatographique sur la composition d'une tache globale sur papier.

SUMMARY

Refractive index and eutectic melting temperature of binary systems, together lead to specific identification of organic individuals and isomers. A number of vitamins and amino acids have been experimented with to that purpose. The result is that analysis of an entire spot of amino acids on paper becomes easy owing to these properties. An example using glumatic acids shows that better results on the composition of an entire spot on paper can be obtained by this analysis than by chromatographic R_F values.

ZUSAMMENFASSUNG

Der Brechungsexponent und die eutektische Schmelztemperatur von binären Gemischen, sind zwei Eigenschaften, welche eine spezifische Identifikation der organischen Körper und der Isomeren erlauben. Sie wurden zu diesem Zwecke an einer gewissen Anzahl Vitaminen und Aminosäuren ausprobiert. Daraus resultiert, dass die Analyse eines globalen Fleckens von Aminosäuren auf Papier, dank dieser Eigenschaften einfach wird. Ein Beispiel für die Glutaminsäuren zeigt, dass diese Analyse besser als der chromatographische R_F-Wert über die Zusammensetzung eines globalen Fleckens auf Papier Aufschluss gibt.

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DIETHYLENETETRA-AMMONIUM SULPHATOCERATE AS VOLUMETRIC REAGENT

I. IODINE MONOCHLORIDE METHOD

by

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The salts of quadrivalent cerium are the most versatile of the strong oxidizing agents, which may be used as standard solutions. Quadrivalent cerium salts are yellow and on reduction form trivalent colourless cerous salts. Cerate solutions are usually made up to approximately the concentration desired and then standardized with arsenious acid, sodium oxalate, ferrous ethylenediamine sulphate or electrolytic iron.

This paper describes the preparation of diethylenetetra-ammonium sulphatocerate, $[Ce(NH_2–CH_2–CH_2–NH_2)_2](SO_4)_2.2H_2SO_4.7H_2O$, and its use as an oxidimetric standard in volumetric analysis.

In the presence of hydrochloric acid, diethylenetetra-ammonium sulphatocerate has been used as a volumetric reagent for the determination of potassium iodide, ferrous ammonium sulphate, arsenious oxide, stannous chloride, hydrazine sulphate, thallous chloride, hydroquinone and potassium ferrocyanide.

Preparation of diethylenetetra-ammonium sulphatocerate

Ceric sulphate (E. Merck) and ethylenediamine hydrate (E. Merck) in equimolecular proportions were dissolved in 2*N* and 4*N* sulphuric acid respectively. The two solutions were mixed together, concentrated and allowed to stand overnight, when deep orange coloured crystals were formed. These crystals were filtered on a Buchner funnel, washed thoroughly with absolute alcohol and dried in an electric oven at 60° C. A sample of diethylenetetra-ammonium sulphatocerate was analysed and found to contain Ce, 18.09%; C, 6.19%; N, 7.20%; S, 16.52%. The calculated values for the formula, $[Ce(NH_2–CH_2–CH_2–NH_2)_2]\ (SO_4)_2.\ 2H_2SO_4.7H_2O$, are Ce, 18.09%; C, 6.20%; N, 7.23%; S, 16.56%.

Diethylenetetra-ammonium sulphatocerate prepared by this method showed no tendency to undergo any decomposition, deliquescence or efflorescence. A sample of this compound left loosely covered in the laboratory for about six months showed no change in composition. The compound is easy to prepare and preserve in the pure state. Its solution may be heated to boiling without decomposition. As an oxidant it has a high molecular or equivalent weight (774.7).

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EXPERIMENTAL

A known amount of each substance was transferred to a conical flask and about 25 ml of water, 50 ml of concentrated hydrochloric acid, 5 ml of 0.01*M* iodine monochloride and 5 ml of chloroform were added. The mixture was cooled to room temperature and titrated against standard diethylenetetra-ammonium sulphatocerate. The reagent was added from a burette until the solution, which was coloured with iodine, became pale yellow and the chloroform layer acquired a purple colour due to iodine. The conical flask was stoppered and vigorously shaken during the titration. Addition of small volumes of the sulphatocerate solution was continued, shaking vigorously after each addition until the chloroform layer was faintly violet. The sulphatocerate was then added dropwise, with shaking after the addition of each drop, until the chloroform layer became very pale yellow. The end-point was very sharp.

The standard solution of diethylenetetra-ammonium sulphatocerate was prepared by dissolving its known weight in 2*N* sulphuric acid solution and making up to a known volume with the acid. In these titrations normality of the solution with respect to hydrochloric acid was kept between 5*N* to 7*N*. Several titrations were performed in each case. From the volume of the sulphatocerate used, corresponding to the end-point in each titration, the amount of each substance was calculated. From the results given in Tables I-VIII it may be concluded that diethylenetetra-ammonium sulphatocerate (DTS) is an oxidimetric standard for the determination of potassium iodide, ferrous ammonium sulphate, arsenious oxide, stannous chloride, hydrazine sulphate, thallous chloride, hydroquinone and potassium ferrocyanide.

TABLE I

POTASSIUM IODIDE $(I^- \rightarrow I^+)$

KI taken g	*0.02N DTS used* ml	*KI found* g
0.0154	9.30	0.0154
0.0199	12.00	0.0199
0.0257	15.50	0.0257
0.0299	18.00	0.0299
0.0352	21.20	0.0352

TABLE II

FERROUS AMMONIUM SULPHATE $(Fe^{+2} \rightarrow Fe^{+3})$

$FeSO_4.(NH_4)_2SO_4.6H_2O$ *taken* g	*0.02N DTS used* ml	$FeSO_4.(NH_4)_2SO_4.6H_2O$ *found* g
0.0510	6.50	0.0510
0.0729	9.30	0.0729
0.0941	11.95	0.0937
0.1113	14.15	0.1110
0.1330	16.95	0.1329

TABLE III

ARSENIOUS OXIDE $(As^{+3} \rightarrow As^{+5})$

As_2O_3 *taken* g	*0.02N DTS used* ml	As_2O_3 *found* g
0.0109	11.00	0.0109
0.0132	14.35	0.0132
0.0168	17.05	0.0169
0.0201	20.30	0.0201
0.0228	23.00	0.0228

TABLE IV

STANNOUS CHLORIDE $(Sn^{+2} \rightarrow Sn^{+4})$

$SnCl_2.2H_2O$ *taken* g	*0.02N DTS used* ml	$SnCl_2.2H_2O$ *found* g
0.0181	8.00	0.0181
0.0280	12.35	0.0279
0.0338	15.00	0.0338
0.0406	17.95	0.0405
0.0474	20.95	0.0473

TABLE V

HYDRAZINE SULPHATE $(N_2H_4 \rightarrow N_2 + 4H^+)$

$N_2H_4.H_2SO_4$ *taken* g	*0.02N DTS used* ml	$N_2H_4.H_2SO_4$ *found* g
0.0049	7.50	0.0049
0.0074	11.25	0.0073
0.0105	16.15	0.0105
0.0128	19.70	0.0128
0.0143	22.00	0.0143

TABLE VI

THALLOUS CHLORIDE $(Tl^+ \rightarrow Tl^{+3})$

TlCl taken g	*0.02N DTS used* ml	*TlCl found* g
0.0240	10.00	0.0240
0.0288	12.00	0.0288
0.0384	16.00	0.0384
0.0504	21.00	0.0504
0.0576	24.00	0.0576

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TABLE VII

HYDROQUINONE ($C_6H_4(OH)_2 \rightarrow C_6H_4O_2 + 2H^+$)

$C_6H_4(OH)_2$ taken g	0.02N DTS used ml	$C_6H_4(OH)_2$ found g
0.0091	8.25	0.0091
0.0129	11.65	0.0128
0.0185	16.80	0.0185
0.0211	19.15	0.0211
0.0259	23.40	0.0258

TABLE VIII

POTASSIUM FERROCYANIDE
($[Fe(CN)_6]^{-4} \rightarrow [Fe(CN)_6]^{-3}$)

$K_4[Fe(CN)_6]$ taken g	0.02N DTS used ml	$K_4[Fe(CN)_6]$ found g
0.0591	7.00	0.0591
0.1014	12.05	0.1017
0.1309	15.50	0.1309
0.1605	19.00	0.1605
0.1858	22.05	0.1862

SUMMARY

The method of preparation of diethylenetetra-ammonium sulphatocerate is described. This substance has been used as an oxidant to determine potassium iodide, ferrous ammonium sulphate, arsenious oxide, stannous chloride, hydrazine sulphate, thallous chloride, hydroquinone and potassium ferrocyanide by a volumetric method, using iodine monochloride as catalyst and pre-oxidizer. During these titrations, normality of the solution with respect to hydrochloric acid has been kept at about 6*N*. Chloroform is used as an indicator. It is coloured pink owing to the liberation of iodine during the titration and becomes very pale yellow at the end-point because of the formation of iodine monochloride.

RÉSUMÉ

Une méthode de préparation du sulfate de di(éthylènediamino)-cérium(IV) est décrite. Le réactif a été utilisé comme oxydant pour le dosage de l'iodure de potassium, du sulfate de fer(II) et d'ammonium, de l'anhydride arsénieux, du chlorure d'étain(II), du sulfate d'hydrazine, du chlorure de thallium(I), de l'hydroquinone et du ferrocyanure de potassium par volumétrie, en présence de monochlorure d'iode comme catalyseur et pré-oxydant. Pendant ces titrations, la normalité de la solution en acide chlorhydrique est maintenue à 6. Le chloroforme est utilisé comme indicateur. Il se colore en violet par l'iode libéré durant le titrage et devient jaune très pâle au point final, par formation de monochlorure d'iode.

ZUSAMMENFASSUNG

Die Autoren beschreiben eine Methode zur Darstellung von Cer(IV)di(äthylendiamin) sulfat. Das Reagenz wird, in Gegenwart von Jodmonochlorid als Katalysator und voroxydierendes Mittel, als Oxydationsmittel zur volumetrischen Bestimmung folgender Substanzen verwendet: Kaliumjodid, Eisen(II)sulfat, Ammoniumsulfat, arsenige Säure, Zinn(II)chlorid, Hydrazinsulfat, Thallium(I)chlorid, Hydrochinon, Kaliumferrocyanid. Während dieser Titrationen wird die Normalität der Salzsäurelösung bei sechs konstant gehalten. Das Chloroform wird als Indikator benützt. Es färbt sich violett durch das während der Titration freigewordene Jod und wird am Endpunkt blass gelb durch die Bildung von Monochlorid.

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FLUOROBERYLLATES IN CHEMICAL ANALYSIS

by

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Extensive work of RAY and his co-workers[1] showed close analogy between sulphates and fluoroberyllates. RAY[2] showed that barium fluoroberyllate, having the composition $Ba[BeF_4]$, is insoluble in water and in dilute acids and has the same crystal structure as barium sulphate.

An investigation was made of the use of a soluble fluoroberyllate as precipitating agent in the quantitative estimation of barium. This was done in order to study the analogy of sulphates and fluoroberyllates in their analytical reactions and not with any intention of replacing sulphates by fluoroberyllates in conventional analysis.

It was decided from the beginning to use a neutral solution for precipitation to avoid platinum vessels. With neutral solution sintered glass crucibles can be used for filtration.

Preliminary experiments to precipitate a neutral barium chloride solution by ammonium fluoroberyllate solution gave low results due to some co-precipitated barium fluoride. The fluoride ion was furnished by dissociation of the fluoroberyllate.

In presence of ethylenediaminetetraacetic acid (complexone) barium fluoride does not precipitate in neutral solution though barium fluoroberyllate does precipitate. Under these conditions lead does not precipitate and a separation of barium and lead can be achieved.

PRIBIL AND MARICOVA[3] separated barium from lead and many other elements by precipitating barium sulphate in presence of complexone. Barium sulphate dissolves in ammoniacal complexone solution from which it can be reprecipitated by acidification. Barium fluoroberyllate on treatment with ammoniacal complexone solution partially hydrolyzed to beryllium hydroxide and therefore pure barium fluoroberyllate could not be reprecipitated on acidification.

Reagents and chemicals

1. Complexone — disodium ethylenediaminetetraacetic acid A.R. 10% solution was used.
2. Ammonium fluoroberyllate — recrystallized ammonium fluoroberyllate prepared according to the method of RAY. 10% solution was used.
3. Barium chloride stock solution prepared from A.R. quality barium chloride. Strength determined gravimetrically as barium sulphate.
4. Lead nitrate stock solution — prepared from A.R. quality lead nitrate. Strength determined gravimetrically as lead sulphate.

All other reagents were A.R. grade

Procedure

The acidic solution containing barium was treated with 10 ml complexone diluted to 200 ml and adjusted to pH 6 with dilute ammonium hydroxide, methyl red being used as indicator. The solution was heated to boiling and 10 ml of ammonium fluoroberyllate solution was added dropwise with constant stirring. The solution was allowed to stand on a hot plate for few minutes, cooled to room temperature, filtered through a sintered glass crucible and washed thoroughly with cold water. The precipitate was dried at 110° C and weighed as $BaBeF_4$ — containing 61.765% barium. The results are shown in Table I.

TABLE I

Barium present mg	*Ba[BeF$_4$] precipitated* mg	*Barium found* mg	*Error* mg
27.32	44.3	27.36	+0.04
27.32	44.2	27.30	−0.02
40.98	66.5	41.04	+0.06
40.98	66.6	41.03	+0.05
54.64	88.5	54.66	+0.02
54.64	88.6	54.73	+0.09
68.30	110.6	68.31	+0.01
68.30	110.4	68.20	−0.10

The same procedure was adopted for separation of barium from lead. Results are given in Table II.

TABLE II

Barium present mg	*Lead present* mg	*Barium found* mg	*Error* mg
68.30	6.96	68.31	+0.01
68.30	6.96	68.31	+0.01
68.30	34.81	68.20	−0.10
68.30	34.81	68.20	−0.10
68.30	69.62	68.20	−0.10
68.30	69.62	68.20	−0.10
68.30	139.24	68.20	−0.10
68.30	139.24	68.31	+0.01
68.30	696.2	68.31	+0.01
68.30	696.2	68.20	−0.10

The crucibles were cleaned by heating with a mixture of boric acid and hydrochloric acid.

The authors are indebted to Prof. N. N. Ray, D. Sc. of Presidency College, Calcutta, for his kind interest in the work and to Mr. S. Banerjee, M. Sc., of the College of Engineering and Technology, Jadavpur, Calcutta for various suggestions and help during the course of investigations. One of us (A.K.G.) is grateful to the Ministry of Education, Govt. of India, for a scholarship.

SUMMARY

Barium can be precipitated as barium fluoroberyllate, $Ba[BeF_4]$, with ammonium fluoroberyllate in the presence of ethylenediaminetetraacetic acid at pH 6-7. Lead does not precipitate under these conditions and a good separation can be effected. The precipitate is dried at 110° C and weighed.

RÉSUMÉ

Le baryum peut être précipité comme fluoglucinate Ba[BeF_4], au moyen de fluoglucinate d'ammonium, en présence d'acide éthylènediaminetétraacétique, au pH 6-7. Le plomb ne précipite pas dans ces conditions, ce qui permet une bonne séparation baryum-plomb. Le précipité obtenu est séché à 110° C et pesé.

ZUSAMMENFASSUNG

Das Barium kann als Fluoroglucinat Ba[BeF_4] mittels Ammonium Fluoroglucinat, in Gegenwart von Äthylendiamintetraessigsäure bei pH 6-7 ausgefällt werden. Das Blei fällt unter diesen Bedingungen nicht aus, was eine gute Trennung Blei-Barium erlaubt. Der erhaltene Niederschlag wird bei 110° getrocknet und gewogen.

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COPRECIPITATION OF COBALT WITH NICKEL DIMETHYLGLYOXIME

by

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INTRODUCTION

In 1905, TSCHUGAEFF[1] discovered that dimethylglyoxime reacts with the nickel(II) ion to give a brilliant red insoluble compound. His work was verified and extended by KRAUT[2], who showed that as little as one microgram of nickel could be detected by this reaction. The use of dimethylglyoxime for the gravimetric determination of nickel was first proposed by BRUNCK[3], who investigated the completeness of precipitation both from ammoniacal solution and from solutions buffered with the acetate ion. Since these early investigations, many modifications have been proposed, most of them dealing with methods to prevent the coprecipitation of other metal ions[4,5]. The red precipitate formed by the reaction of dimethylglyoxime with nickel ion has been shown to have a composition $Ni(C_4H_7O_2N_2)_2$. Other investigators have shown that the compound is a planar first order inner complex[4].

Almost without exception, articles in the literature appear to agree that dimethylglyoxime will completely separate nickel from cobalt under proper conditions[5]. It has been reported that when large amounts of nickel are precipitated in the presence of small amounts of cobalt, the precipitation with dimethylglyoxime from an ammoniacal solution gives a clean separation. Most authors agree that when cobalt is present an excess of dimethylglyoxime sufficient to complex all the cobalt must be added[4]. BRUNCK recommended an amount of dimethylglyoxime about five times the amount of nickel present with no mention of any relation to the quantity of cobalt present[7].

Large amounts of cobalt and copper seem to retard the precipitation of nickel dimethylglyoxime, but the difficulty may be overcome by using excess dimethylglyoxime and by allowing extra time for precipitation[8]. In ammoniacal solution, the cobalt dimethylglyoxime complex appears to retard the precipitation of small amounts of nickel[5], but this difficulty can be avoided by using the acetate method[6,8,9]. The nickel precipitate is also often peptized by the cobalt complex, making filtration difficult[5]. Macro amounts of nickel have been precipitated from homogeneous solution containing dimethylglyoxime and urea. Hydrolysis of the latter compound was employed to adjust the pH value.

The cobalt(II)-dimethylglyoxime complex has been characterized by the method of continuous variations, which indicated that there is a cobalt-to-dimethylglyoxime ratio of 1:2 [12]. Since the cobalt complex is soluble, it is probably a second order complex. CAMBI AND CORISELLI state that cobalt(II) goes over very readily to cobalt(III) in the presence of dimethylglyoxime[3]. Many complexes, some soluble, some insoluble, have been identified following the oxidation of cobalt(II) to cobalt(III) in the presence of dimethylglyoxime and air[3].

In this work it was proposed to investigate the coprecipitation of cobalt with nickel in the various dimethylglyoxime procedures when the cobalt is present in small amounts. The determination of the cobalt was to be facilitated by labeling it with its radioisotope cobalt-60.

EXPERIMENTAL

Chemicals and apparatus

Five millicuries of cobalt-60 as 3.1 mg of cobalt(II) chloride was obtained from Oak Ridge National Laboratory. This was used to prepare 50 ml of a standard solution containing 6.12 mg of cobalt per ml in the form of cobalt(II) sulfate. The gamma ray radioactivities of various cobalt-60-containing solutions were measured in a specially designed glass sample holder with a volume of 15 ml. This holder was placed in constant geometry near a Model SC-1B Nuclear Research Corporation Scintillation Counter which was attached to a conventional scaler and timer.

Jacketed beakers, with constant-temperature water flowing through the jackets, were used for all precipitations. The temperature control was in all cases within ± 2°. Samples were stirred with magnetic stirrers.

The nickel solution used in all precipitations was one of nickel(II) sulfate containing 5.76 mg of nickel per ml. The dimethylglyoxime solution was prepared by dissolving 7.5 g of the reagent grade material in 1 l of 95% ethanol. All other chemicals were of reagent grade quality.

The ammonia method

Ten ml of the nickel sulfate solution (57.6 mg of nickel), 0.1 ml of radioactive cobalt sulfate solution (612 μg of cobalt), and 10 ml of distilled water were placed in the beaker for each determination. Rapid addition studies were made by dumping 40 ml of the dimethylglyoxime solution and 5 ml of concentrated ammonium hydroxide into the solution. These studies were carried out at 25° and at 85°. Slow addition studies were made by adding 40 ml of the dimethylglyoxime to the solution followed by 5 ml of concentrated ammonium hydroxide added dropwise at the rate of 1 drop per sec, the latter addition bringing about the precipitation.

Following addition of the reagents, the precipitates were digested for various times. They were then separated by filtration, dissolved in concentrated hydrochloric acid, diluted to 25 ml total volume, and 15 ml was placed in the sample holder and counted. Comparison with a standard cobalt sample allowed the amount of coprecipitated cobalt to be calculated. The filtrates from the precipitations were all tested for completeness of precipitation by the use of a large excess of ammonia and dimethylglyoxime solutions.

The acetate method

The same conditions as to the amounts of nickel, cobalt and dimethylglyoxime, mode of reagent addition, and treatment of the samples after precipitation prevailed during the acetate precipitations as during those in ammoniacal media. However, instead of ammonium hydroxide, 15 ml of 10% sodium acetate solution was added, followed by 1 g of solid sodium acetate.

Results

For each determination at a given temperature, addition time, and digestion time, at least five runs were made. The average of these runs was determined and the standard deviation of the average was calculated. The result of each determination was expressed as the average with the reliable error (90% confidence level[14]) affixed. In all cases of rejected data, the method of PIERCE AND CHAUVENET[15] was the basis. Tables I and II present the results obtained in the ammonia method, and Tables III and IV present those obtained by the acetate method.

TABLE I

COBALT COPRECIPITATED WITH $Ni(dmg)_2$ BY THE AMMONIA METHOD AT 25°

Reagent addition	*Digestion (min)*	*Cobalt (µg)*
slow	0	26.6 ± 7.9
slow	30	2.6 ± 1.3
rapid	0	52.2 ± 9.9
rapid	30	8.9 ± 4.4
rapid	90	4.6 ± 2.0
rapid	180	2.6 ± 2.1
rapid	300	2.9 ± 1.1

TABLE II

COBALT COPRECIPITATED WITH $Ni(dmg)_2$ BY THE AMMONIA METHOD AT 85°

Reagent addition	*Digestion (min)*	*Cobalt (µg)*
slow	0	4.6 ± 3.1
slow	30	5.9 ± 2.7
rapid	0	4.1 ± 3.0
rapid	30	4.5 ± 2.2
rapid	60	5.3 ± 2.3
rapid	120	11.2 ± 3.6
rapid	210	11.3 ± 3.8
rapid	300	20.8 ± 2.1

TABLE III

COBALT COPRECIPITATED WITH $Ni(dmg)_2$ BY THE ACETATE METHOD AT 25°

Reagent addition	*Digestion (min)*	*Cobalt (µg)*
slow	0	7.1 ± 2.3
slow	30	5.3 ± 3.1
rapid	0	14.0 ± 1.6
rapid	30	2.9 ± 2.5
rapid	60	7.5 ± 1.5
rapid	120	10.8 ± 1.9
rapid	210	7.0 ± 1.5
rapid	300	6.9 ± 3.9

TABLE IV

COBALT COPRECIPITATED WITH $Ni(dmg)_2$ BY THE ACETATE METHOD AT 85°

Reagent addition	*Digestion (min)*	*Cobalt (µg)*
slow	0	4.6 ± 1.9
slow	30	16.1 ± 4.0
rapid	0	5.0 ± 2.5
rapid	30	14.1 ± 4.2
rapid	60	17.9 ± 1.7
rapid	120	17.1 ± 4.8
rapid	210	128.0 ± 10.9
rapid	300	125.0 ± 12.4

DISCUSSION

The amount of cobalt coprecipitated with the nickel dimethylglyoxime by the ammonia method at 25° is very large for the determinations (both slow and rapid) in which the precipitates were not digested after addition of the reagents. However, as the digestion time increased, the carried cobalt decreases to an almost constant amount. The precipitates which were not stirred after completion of the precipitation were gelatinous and difficult to filter, but with longer stirring times the material became more curdy or mealy, and consequently it was much easier to filter. The relatively large amount of cobalt coprecipitated initially is believed to be due to a trapping process and to adsorption on the large surface area presented by the gelatinous precipitate. With longer digestion times, the precipitate reforms, probably through the process of Ostwald ripening, releasing the trapped cobalt, and also decreasing the surface area[16]. It is possible that the small amount of cobalt which could not be removed even by prolonged digestion was in solid solution with the nickel dimethylglyoxime, the cobalt occupying sites which would ordinarily be occupied by nickel. The formation of such a solid solution might be easy since the cobalt(II) complex may be similar to that of nickel[12,13,17,18,19].

The coprecipitation of cobalt in the ammonia method at 85° shows a constant increase in the amount of cobalt as the digestion time increases. As the precipitate formed, it was gelatinous, but it became mealy very quickly (within one minute after the addition of the reagents). Then as time went on, the small mealy clumps gathered into larger more slimy looking aggregates, the size growing as the time increased. It is believed that no initially high value for coprecipitated cobalt was observed because the transformation from gelatinous to mealy precipitate occurred before separation of the solution and precipitate could be effected. The increase in carried cobalt with time, as well as the change in form of the precipitate may be related to the loss of alcohol at this temperature, and the resulting decrease in the solubility of dimethylglyoxime.

The initially high value of coprecipitated cobalt in the acetate method at 25° may again be related to the character of the precipitate, which was very gelatinous at the beginning. With increased digestion time the precipitate became mealy, the clump size remaining fairly constant. The decrease in cobalt coprecipitated with increased digestion time could again be explained by this transformation in the appearance of the precipitate. There seems to be no obvious explanation for the later rise and subsequent drop in the amount of cobalt carried as the digestion time goes from 60 to 300 minutes. This behavior may be related to a valence change of cobalt from (II) to (III) and/or a change in the form of the cobalt dimethylglyoxime complex. CAMBI AND CORISELLI state that cobalt(II) goes to cobalt(III) quite easily under these conditions[13]. Numerous complexes of cobalt(III) with dimethylglyoxime have been reported; some are insoluble, which might alter the coprecipitation picture markedly[13,17,18,19].

Initially the amount of cobalt brought down by the acetate method at 85° is relatively small. However, as time goes on, this amount increases, reaching a very high value after 120 minutes. An explanation similar to that given in the ammonia procedure at 85° would seem to be applicable here. Valence changes such as those postulated in the previous paragraph may have occurred; if they did, however, their effects could have been masked by the rapid rise in coprecipitation produced by the precipitate form at this temperature.

In all cases, the effect of slow reagent addition was to accelerate the phenomena which would occur in the rapid addition procedure. Of those investigated, the best condition for the precipitation of nickel in the presence of small amounts of cobalt by the dimethylglyoxime method seems to be the slow addition of ammonia followed by a digestion for 30 minutes, all processes being carried out at 25°.

SUMMARY

The coprecipitation of cobalt with nickel precipitated as the dimethylglyoxime complex has been investigated under various conditions. Precipitations were carried out in ammonia and acetate solutions, at 25° and 85°, with slow and rapid addition of the solution of the precipitating agent, and with various digestion times. In each experiment, the amount of cobalt was 612 μg and the amount of nickel was 57.6 mg. Of the methods investigated, minimum coprecipitation was achieved by slow addition of ammonia to the acid nickel, cobalt, and dimethylglyoxime solution followed by a 30-minute digestion, all processes being carried out at 25°.

RÉSUMÉ

La coprécipitation du cobalt avec le complexe nickel-diméthylglyoxime a été examinée dans diverses conditions. Les précipitations ont été effectuées en solutions ammoniacales et d'acétate, à 25 et 85°, avec additions lente et rapide de la solution de réactif et avec des digestions de différentes durées. Pour chaque expérience, la teneur en cobalt était de 612 μg et la teneur en nickel de 57.6 mg. On a trouvé que la coprécipitation était la plus faible dans les conditions suivantes: addition lente d'ammoniaque à la solution acide de nickel, cobalt et diméthylglyoxime, suivie d'une digestion de 30 minutes; température de 25° pour toutes les opérations.

ZUSAMMENFASSUNG

Die Kopräzipitation von Kobalt mit dem Komplex Nickel-Dimethylglyoxim wurde unter verschiedenen Bedingungen untersucht. Die Ausfällungen wurden bei 25 und 85° in Ammoniak- und Acetatlösungen ausgeführt mit langsamer und schneller Zugabe der Reagenzlösung und mit Wartezeiten von verschiedener Dauer. Für jedes Experiment war der Gehalt an Kobalt 612 μg und der Gehalt an Nickel 57.6 mg. Man fand, dass die Kopräzipitation unter folgenden Bedingungen am schwächsten war: langsame Zugabe von Ammoniak zu der sauren Lösung von Nickel, Kobalt und Dimethylglyoxim, bei nachheriger Wartezeit von 30 Minuten, Temperatur 25° für alle Operationen.

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SEPARATION OF CALCIUM AND ALUMINUM FROM IRON BY AN ION EXCHANGE METHOD

by

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INTRODUCTION

A method has been worked out for the determination of calcium and aluminum in the presence of iron. Calcium is separated from iron and aluminum by means of an anion exchanger according to the method devised by SAMUELSON, LUNDÉN, AND SCHRAMM[5]. Iron and aluminum are, provided that proper conditions are chosen, taken up quantitatively in a column filled with a resin in the citrate form. Calcium passes into the effluent. The separation of aluminum from iron is based upon the pioneering work by KRAUS AND MOORE[3] on the behavior of different metal ions in concentrated hydrochloric acid. These authors found that in strong hydrochloric acid iron is bound very strongly to an anion exchanger in chloride form whereas aluminum is easily eluted.

In the present work it is shown that the citrate ions left in the column after the removal of the calcium ions do not interfere with the separation of aluminum from iron by elution with concentrated hydrochloric acid. Special precautions have to be taken to obtain a quantitative separation.

The method has been adopted for the analysis of commercial products, *e.g.* lime.

EXPERIMENTAL PART

Ion exchange column

A modified type of ion exchange column used in the present investigation is shown in Fig. 1. This type of column permits the introduction of the elutriant at the bottom of the column through the three-way cock. In other respects the column is of standard type and filled with resin in the usual manner[4].

The strongly basic anion exchanger Dowex 2 was used in all experiments. The particle size was 0.2-0.3 mm and the dimensions of the resin bed 15 × 180 mm. The resin was transformed into the citrate form by passing 300 ml 1*M* citric acid through the column and washing with about 200 ml water. It must be observed that the method does not work when weakly basic resins are used and that aluminum and iron are not taken up quantitatively on a strongly basic anion exchanger if the resin contains a considerable number of weakly basic groups.

Ion exchange procedure

The solution to be analysed is introduced into the funnel A and passed downwards through the resin bed and through the outlet tube B. After washing with water until no calcium ions appear in the effluent, calcium is determined in the collected effluent and washing water. A proper flow rate in both these steps is 2 ml/min. In the experiments performed in the present investigation it was found that about 300 ml water was required in the washing step. It has, however, been observed that different resins of similar quality behave somewhat differently and it is therefore recommended to work with a broad margin of safety and to make control tests when new resins are used. As the distilled water contained traces of impurities the water was deionized before use[4].

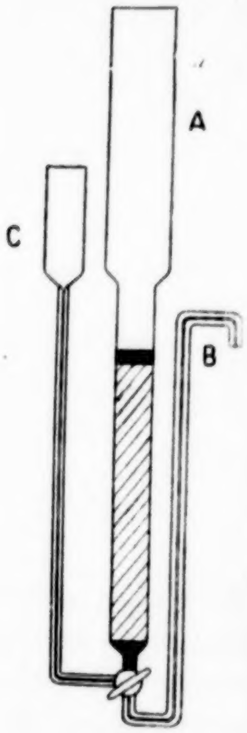

Fig. 1. Ion exchange column.

After the sorption step the funnel C is filled with concentrated hydrochloric acid and, by switching the three-way cock, the acid is forced upwards through the resin bed. In this manner the water left in the column is displaced from the column into the funnel A. Iron and aluminum are to a large extent removed from the column. The solution which appears in the funnel A has a yellow color due to the iron chloride complex.

It must be noted that the glass tube which connects the funnel C with the three-way stopcock must be filled with solution in order to prevent air being forced into the column. If the tube is a capillary it can be simply filled by switching the cock to connect the capillary with the outlet tube and applying gentle suction.

A further amount of concentrated acid (about 75 ml) is placed in the funnel A in such a way that mixing occurs. The cock is switched over to the same position as that during the sorption step and the hydrochloric acid is passed downwards through the resin bed. Iron is readsorbed in the column and the eluate which contains the aluminum is taken out through the outlet tube B. The solution is displaced by means of concentrated hydrochloric acid until aluminum has been eluted quantitatively. About 75 ml is required under the conditions used in the present work. Iron can be eluted by washing with water and $1M$ hydrochloric acid.

It can be mentioned that some modifications in the elution of aluminum have been tried but the method described above is considered to be the simplest.

Analytical methods

In the experiments with mixtures of pure salt solutions, the solutions of calcium chloride, magnesium chloride, and manganese chloride were standardized by gravimetric determinations as sulfate. Aluminum was determined by precipitation with 8-hydroxyquinoline.

Calcium, which was obtained after the sorption step in the effluent, was determined as sulfate after ignition to remove citric acid, addition of sulfuric acid, and heating at 700° C[5]. In some experiments with solutions which in addition contained magnesium and manganese, the sum was determined as sulfate. When manganese was present, the ash was treated with hydrogen peroxide after the ignition and addition of sulfuric acid in order to reduce manganese to the bivalent state.

Aluminum was determined in the eluate after addition of sulfuric acid, evaporation and ignition to remove citric acid. The ash was dissolved by melting with potassium hydrogen sulfate and aluminum determined gravimetrically as oxinate[2].

For a comparison and control of the analyses of lime, aluminum and iron have been determined colorimetrically with ferron[1] and the sum by precipitation as hydroxide. In the lime analysis, 2-3 g lime was treated with 15 ml water and stirred thoroughly to wet the powder. It was then treated with 20 ml of concentrated hydrochloric acid and evaporated to dryness with an infrared lamp. After heating for one hour at 185° C, the sample was dissolved in hydrochloric acid and silica removed by filtration in the usual manner. After washing, the filtrate was evaporated to dryness on a water bath. The residue was dissolved in water and 5 ml $1M$ hydrochloric acid added to complete dissolution. The solution was diluted to 250 ml and 20 ml taken for each determination. A large excess of acid has to be avoided[5].

RESULTS AND DISCUSSION

The results from experiments performed with solutions to which known amounts of calcium chloride, aluminum chloride, and iron chloride had been added are given in Table I. In some of the solutions, magnesium chloride and manganese chloride were also present. As may be seen from the table, calcium is recovered quantitatively

TABLE I

ANALYSIS OF SOLUTIONS CONTAINING KNOWN AMOUNTS OF Ca, Mg, Mn, Al, AND Fe

Added					*Found*			
					Ca + Mg + Mn		*Al*	
Fe mmol	*Ca mmol*	*Mg mmol*	*Mn mmol*	*Al mmol*	*mmol*)*	*rel. error* %	*mmol*	*rel. error* %
0.5	4.985			0.497	4.981	−0.1	0.496	−0.2
0.5	1.621			0.499	1.617	−0.2	0.498	−0.2
0.5	1.621			0.499	1.614	−0.4	0.497	−0.4
0.5	3.988			0.497	3.987	0.0	0.497	0.0
0.5	1.994			0.497	1.992	−0.1	0.498	+0.2
0.5	5.982			0.497	5.976	−0.1	0.495	−0.4
0.5	2.991			0.199	2.990	0.0	0.200	+0.5
0.5		2.002		0.497	2.006	+0.2	0.497	0.0
0.5		3.003		0.497	3.004	0.0	0.495	−0.4
0.5		4.004		0.497	4.001	−0.1	0.495	−0.4
0.5	2.991	3.003		0.497	6.003	+0.2	0.496	−0.2
0.5	2.991		0.500	0.100	3.500	+0.3	0.100	0.0
0.1	5.982		0.050	0.199	6.024	−0.1	0.200	+0.5
0.1	5.982		0.050	0.050	6.030	0.0	0.050	0.0

* For the samples which contain Mg or Mn as well as Ca, these values are calculated from the weight of the sulfates using an average molecular weight calculated from the composition of the sample.

in the effluent from the column. Magnesium and manganese are also quantitatively recovered. The maximum relative error is 0.4%. The separation of aluminum from iron by elution with hydrochloric acid is also excellent. The greatest difference between the added and found amounts of aluminum is 0.002 mmol and the maximum relative error 0.5%. In separate experiments, colorimetric tests were used to check that no iron appeared in the eluate. It was found that less than 10^{-4} mmol iron was present in the eluate.

Aluminum has been determined in four different samples of burnt lime. The proposed ion exchange method has been compared with the usual difference method in which the sum of Al_2O_3 and Fe_2O_3 is determined by precipitation with ammonia and Fe_2O_3 colorimetrically. Furthermore, determinations of aluminum have been performed according to the direct spectrophotometric method with ferron[1]. The same reagent has been used in the colorimetric determination of iron. The results are given in Table II. The results from the gravimetric determination of silica and the determination of calcium plus magnesium (calculated as CaO) according to the ion exchange method are included in the table.

TABLE II

ANALYSIS OF BURNT LIME

SiO_2 % *gravim.*	CaO % *ion exchange*	$Al_2O_3 + Fe_2O_3$ % *gravim.*	Fe_2O_3 % *ferron*		Al_2O_3 % *by difference*	Al_2O_3 % *ferron*		Al_2O_3 % *ion exchange*	
1.84	94.6	0.49	0.17	0.18	0.31	0.28	0.31	0.25	0.26
1.55	92.2	0.62	0.19	0.18	0.43	0.43	0.43	0.42	0.40
1.84	93.3	0.61	0.20	0.23	0.39	0.42	0.36	0.38	0.37
2.67	91.9	0.75	0.24	0.32	0.48	0.43	0.46	0.41	0.42

As can be seen from the table, the proposed ion exchange method gives reproducible results for Al_2O_3 also in samples containing a large excess of calcium. The agreement between the three methods is rather satisfactory. The accuracy of the ion exchange method can be increased by using larger samples but this will of course make the operation more time-consuming.

It can also be mentioned that the method has been used for the determination of aluminum in silica, which contained in addition sodium, calcium, and iron. In two analyses, the ion exchange method gave 2.60% and 2.61% Al_2O_3 whereas the difference method gave 2.65% and 2.67%. In this case iron was determined by permanganate titration. It is believed that the proposed ion exchange method is more accurate as it is difficult to remove the last traces of silica which interfere in the difference method.

From the data presented above, it is obvious that the proposed ion exchange method can be used to advantage for the determination of aluminum, calcium, and magnesium in the presence of iron. Manganese behaves in the same manner as calcium and magnesium and does not interfere with the determination of aluminum. In samples containing considerable amounts of iron and aluminum, the proposed procedure seems to be more accurate than the methods generally used at present. The method is also applicable when only small amounts of iron and aluminum are present. As in most other applications of the ion exchange technique the proposed procedure is well suited for routine analyses as several columns can be operated simultaneously. The separation of the sample into three groups, (a) calcium, magnesium, and manganese, (b) aluminum, (c) iron, requires about 4 hours, the time for regeneration of the column not being included.

In the present investigation, most work has been devoted to the determination of aluminum after the separation from iron, calcium, magnesium, and manganese. The separation of calcium and magnesium from iron, aluminum and also other metals by the citrate form of an anion exchanger has been dealt with in detail in the earlier paper[5]. Instead of the gravimetric determination of calcium and magnesium as sulfate after the ion exchange separation from iron and aluminum, other gravimetric or titrimetric methods can of course be used.

We gratefully acknowledge the financial support for this research received from Statens Tekniska Forskningsråd and Chalmerska Forskningsfonden.

SUMMARY

An ion exchange method has been worked out for the separation of calcium and aluminum from iron. In the first step iron and aluminum are taken up in a column filled with an anion exchanger in the citrate form, whereas calcium passes into the effluent. Subsequently, aluminum is eluted by means of concentrated hydrochloric acid.

The method has been adapted to the analysis of lime.

RÉSUMÉ

Une méthode par échange d'ions a été établie pour la séparation du calcium et de l'aluminium du fer. Le fer et l'aluminium sont d'abord retenus sur une colonne remplie avec un échangeur d'anions, sous forme de citrates, tandis que le calcium passe dans l'éluat. L'aluminium est élué par l'acide chlorhydrique concentré.

Cette méthode a été appliquée à l'analyse de la chaux.

ZUSAMMENFASSUNG

Eine Ionenaustauschmethode für die Trennung von Calcium und Aluminium von Eisen wurde ausgearbeitet. In der ersten Stufe werden Eisen und Aluminium in einer Austauschsäule mit

einem Anionenaustauscher in Citratform aufgenommen, während Calcium in den Durchlauf geht. Danach wird Aluminium mit konzentrierter Salzsäure eluiert.

Die Methode wurde für Kalkanalysen verwendet.

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THE SEPARATION OF MOLYBDENUM VALENCIES BY PAPER CHROMATOGRAPHY

PART II[1]

by

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INTRODUCTION

Molybdenum has been recognized as an essential element of plant metabolism since the work of STEINBERG[2], and ARNON AND STOUT[3]. NICHOLAS AND NASON[4] have shown that the metal is an essential constituent of the enzyme nitrate reductase, and that a change in the valency of the metal takes place during the enzymic reduction of nitrate to nitrite. A method for separating the valency states of molybdenum was necessary in order to determine the valency changes undergone in the metabolism of micro-organisms and higher plants[5]. The separations were achieved using paper chromatography.

The quantitative separation of Mo^{VI} and Mo^{V} as thiocyanates has already been described[1]. The present work deals with the separation of hexa- and pentavalent molybdenum as oxine complexes, and of pentavalent and trivalent molybdenum.

EXPERIMENTAL

Separation of Mo^{VI} and Mo^{V} as oxinates

Mo^{VI} oxinate was prepared by mixing a solution of sodium molybdate dihydrate (1 g in 10 ml water), acidified with 2*N* hydrochloric acid (5 ml), and 8-hydroxyquinoline in ethanol (2 g in 20 ml). The mixture was heated and filtered through a Büchner funnel using Whatman No. 1 paper, and the bright yellow residue washed with water and ethanol and dried. The solid was recrystallized by allowing a hot filtered chloroform solution to stand overnight in the refrigerator, filtering off the deposited solid and washing it with ether. The complex was soluble to a small extent in acetone and chloroform, but almost insoluble in other organic solvents and water. Absorption maxima at 250 mμ and 370 mμ, and a minimum at 280 mμ were obtained with a chloroform solution as shown in Fig 1.

If excess of ethanolic oxine was added to a solution of sodium molybdate acidified with hydrochloric acid, and the mixture shaken with zinc dust, a dark purple colour was produced which on adding water and chloroform could be extracted into the latter.

A compound purporting to be Mo^{V} oxinate, which has not previously been reported, was obtained by (i) the addition of a solution of molybdenum pentachloride in 10*N* hydrochloric acid (0.5 g in 5 ml), which was treated with a little sodium amalgam to reduce traces of Mo^{VI}, to a solution of 8-hydroxyquinoline in ethanol (5 g in 50 ml) followed by 20 ml of water. The reddish-purple solution was allowed to stand for 5-10 minutes, filtered, (Whatman No. 41 paper) and poured into 500 ml of water. The mixture was heated to 50°-60°, filtered through a Büchner funnel (Whatman No. 1 paper), and the dark purple residue washed with cold water, ether and

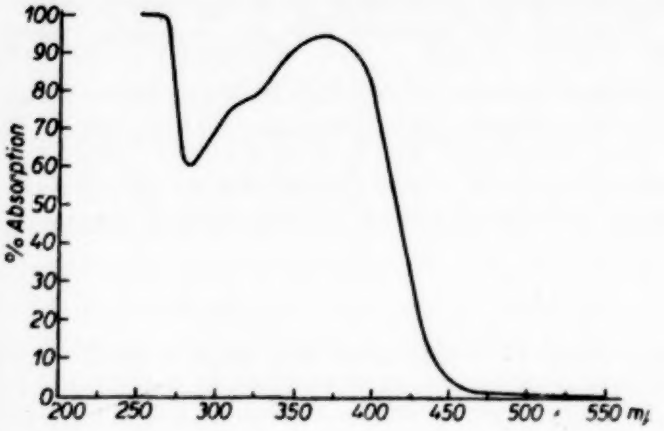

Fig. 1. Mo^{VI} oxine complex: spectrum in the U.V. and visible range.

then dried in an oven at 40°-50°. (ii) dissolving sodium molybdate dihydrate (1 g) and potassium thiocyanate (5 g) in water (20 ml), adding 10*N* hydrochloric acid (20 ml) and warming to 60°-70°. After allowing to stand for 10-15 minutes, the mixture was cooled and shaken with ether (150 ml). The upper ethereal layer was separated, filtered and then added to a solution of oxine in ether (5 g in 10 ml). The dark brown precipitate was filtered off, (Büchner funnel, Whatman No. 1 paper), and boiled with water for a few minutes. The purplish-black residue was filtered off, washed with cold water, ether and dried at 40°-50°. The same compound was formed if solutions of molybdenum pentachloride and oxine in carbon tetrachloride were mixed, and the resulting dark green precipitate was warmed with water for 5-10 min. Method (i) gave the purest product which contained molybdenum and oxine, and only a trace of chloride. The dark purple solid when dissolved in ethanol, acetone, ethyl acetate and chloroform gave reddish-purple solutions, but was almost insoluble in ether, carbon tetrachloride, and water. Absorption maxima at 243 mμ and 540 mμ, and a minimum at 480 mμ were obtained with ethanol solutions. (See Figs. 2 and 3.) The dark brown precipitate obtained in method (ii) contained molybdenum (3.6%), oxine, and thiocyanate, and the dark green precipitate from the carbon tetrachloride reaction contained molybdenum, oxine and chloride.

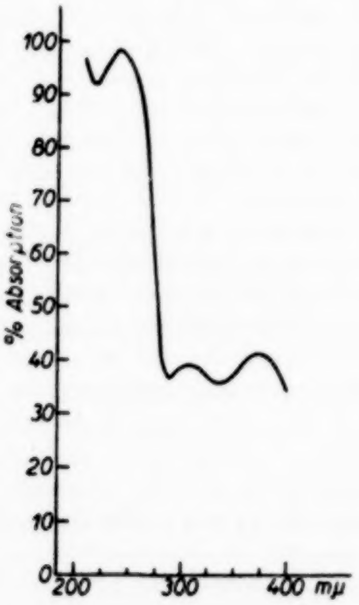

Fig. 2. Mo^{V} oxine complex: U.V. spectrum.

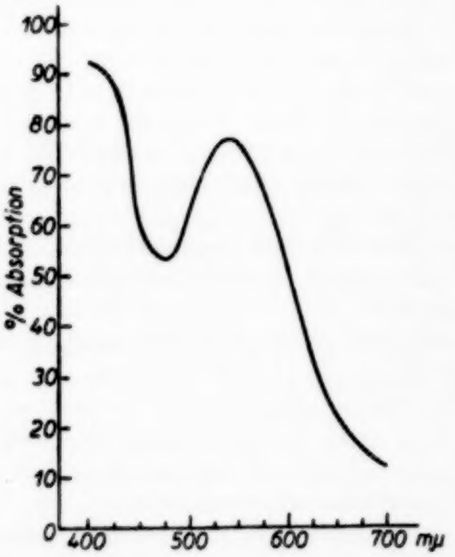

Fig. 3. Mo^{V} oxine complex: visible spectrum.

Analysis of the purple compound gave the following composition: Mo, 19.2% (spectrographic method); C, 50.3%; H, 3.1%; N, 6.25%.

When the complex was warmed with potassium thiocyanate and hydrochloric acid, it was decomposed yielding an orange solution of Mo^{V} thiocyanate. This afforded a colorimetric method for estimating the molybdenum content; 15-20 mg of the complex was heated with 10 ml of a 10% w/v solution of potassium thiocyanate in 2*N* hydrochloric acid and 2 ml of acetone. The orange-red solution was diluted to 100 ml with the thiocyanate reagent, and 5 ml portions extracted with known volumes of ethyl acetate. The colour of the extracts was measured on the Hilger "Spekker" as described previously[1]. A mean value of 22.0% was obtained. A "blank" determination using 15-20 mg of oxine was performed and could be neglected.

It is suggested that the dark purple compound prepared by method (i) may be an "aquo" complex, while the brown and green products obtained by method (ii) are possibly "thiocyanato"- and "chloro"- compounds.

Separations between Mo^{VI} and Mo^{V} as oxinates were obtained on Whatman No. 1 paper strips by placing spots of a mixed chloroform solution on the starting line, allowing the chloroform to evaporate, and eluting with ethanol. R_F values were 0 for Mo^{VI} and 0.9-1.0 for Mo^{V}. The separation was, however, not quantitative as the recoveries of Mo^{V} in experiments on paper chromatograms and cellulose columns, were on average, about 7% below the theoretical values.

Separation of Mo^{V} and Mo^{III}

The preparation of a pure solution of Mo^{III} presented an initial problem. By the electrolysis of a solution of molybdenum trioxide in 10*N* hydrochloric acid at a current of 7-8 amp and using a platinum cathode[6], reduction of the molybdenum below the pentavalent state was not completely effected after about 6 hours operation. Molybdenum trichloride, prepared by heating the pentachloride in hydrogen, was found to be insoluble in all solvents except those which decompose it (*e.g.* nitric acid, sodium hydroxide). A satisfactory method for obtaining an efficient reduction of molybdenum trioxide below the penta-state consisted of adding zinc dust to a mixed solution of sodium molybdate (0.5 g in 5 ml water) and 10*N* hydrochloric acid (10 ml) until the solution ceased to give a red colour when portions were tested with potassium thiocyanate. The solution was then filtered (Whatman No. 41 paper) from excess of zinc dust, and freed from Mo^{V} and zinc as follows:

A cellulose column was prepared by drawing out one end of a piece of glass tubing 30 cm × 1.5 cm (internal diameter) into a jet into which was inserted a plug of glass wool to act as a porous retaining washer. The tube was filled with a suspension of Whatman powdered cellulose in water, and a compressed air supply was attached to the upper end. Water was thereby forced out of the tube, and the cellulose packed tightly and evenly into a column approximately 15 cm in length. 5 ml of the reduced molybdate solution was placed on the column and allowed to soak in; the inner wall of the tube above the cellulose was then wiped with filter paper. Elution was carried out using a solution of thiocyanic acid in ether until at least 15 minutes after the red band of Mo^{V} thiocyanate, together with zinc, had passed out of the column. The eluant was prepared by adding 10*N* hydrochloric acid (40 ml) to a solution of potassium thiocyanate (40 g in 40 ml water) and shaking the mixture with ether (150 ml). The upper ethereal layer was filtered and stored in a refrigerator. A further elution was then carried out using pure ether (to wash out thiocyanic acid) until the eluate was colourless. Distilled water was passed through the column and the orange eluate was collected and warmed to 40°-45° in a stream of carbon dioxide to expel ether. It was then diluted to 100 ml with distilled water.

The chloride solution thus prepared was found to be free of zinc, thiocyanic acid, and Mo^{V} and to possess strong reducing properties. In the presence of sulphanilamide (1% in *N* hydrochloric acid) nitrate was quantitatively reduced to nitrite. The estimation of the nitrite produced was performed colorimetrically using N-(1-naphthyl) ethylenediaminedihydrochloride (0.001% in water)[7].

The molybdenum content of the solution was estimated by mixing 0.5 ml with 10 ml of 10% potassium thiocyanate in 2*N* hydrochloric acid; 2-3 drops of hydrogen peroxide (10 vol.) were added and the red colour allowed to appear and begin to fade. A solution of stannous chloride was then added drop by drop until there was no further deepening of the restored red colour. The solution was extracted with 40-50 ml of ethyl acetate and the extract filtered and measured on the "Spekker" in the usual way.

The valency state of the zinc-reduced solution of Mo was determined as follows: To 1 ml of a solution of sodium molybdate, acidified with hydrochloric acid, and containing 12.5 mg Mo per ml, 5 ml of 10*N* hydrochloric acid and 2.5 ml of water was added. Zinc dust was then added until the solution was orange-brown and ceased to give a red colour when a spot was mixed with potassium thiocyanate on a white tile. When all the zinc had dissolved, the solution was diluted to 100 ml with distilled water. Portions were then mixed with 50 ml of 2*N* sulphuric acid and titrated with standard potassium permanganate solution.

45 ml of reduced molybdate solution ($\equiv$ 5625 μg Mo) required 3.5 ml *N*/20 $KMnO_4$.
(Calc. for $Mo^{III} \rightarrow Mo^{VI} + 3e$, 3.51 ml; for $Mo^{IV} \rightarrow Mo^{VI} + 2e$, 2.34 ml).

40 ml of reduced molybdate solution ($\equiv$ 5000 μg Mo) required 15.6 ml *N*/100 $KMnO_4$.
(Calc. for $Mo^{III} \rightarrow Mo^{VI} + 3e$, 15.62 ml; for $Mo^{IV} \rightarrow Mo^{VI} + 2e$, 10.4 ml).

The molybdenum therefore appears to be trivalent, which agrees with the results obtained by previous workers[6,8,9].

Good qualitative separations between Mo^{III} and Mo^{V} were obtained on acid-washed Whatman No. 1 paper strips using the ether-thiocyanic acid eluant, R_F values being 0 for Mo^{III} and 0.8-0.9 for Mo^{V}. The separations could not be performed quantitatively owing to the oxidation of some of the Mo^{III} to Mo^{V} by thiocyanic acid in the presence of air. The R_F value for Mo^{VI} in this system was 0.8-0.9, but a separation between Mo^{VI} and Mo^{III} could not be performed as these valency states interacted in thiocyanate solution giving Mo^{V}.

When solutions containing trivalent molybdenum and potassium thiocyanate were mixed and shaken with ether, no molybdenum was extracted unless air or hydrogen peroxide was added, when red Mo^{V} thiocyanate passed into the ether. Similarly no molybdenum could be extracted by chloroform from mixed solutions of Mo^{III} in water, and oxine in ethanol unless air was admitted, when reddish purple Mo^{V} oxinate passed into the chloroform layer. These observations suggested that thiocyanate and oxine compounds of trivalent molybdenum, if they exist, are less stable than those of Mo^{V} and are not formed under these conditions. The lack of movement of Mo^{III} in the ether-thiocyanic acid system may be due to the adsorption of the chloride onto the cellulose, while the more covalent molybdenum pentathiocyanate dissolves in, and moves with the organic eluant.

ACKNOWLEDGEMENTS

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SUMMARY

The preparation of Mo^{VI} oxinate and a purported Mo^{V} oxine complex is described. The latter was analysed, and a number of its properties, including separation from the Mo^{VI} compound by paper chromatography, were studied.

The preparation of a solution containing trivalent molybdenum and the separation of this valency from the pentavalent state by chromatography upon cellulose is also described.

Suggestions as to the stability of thiocyanate and oxine compounds of Mo^{III} were made from the results of some extraction experiments performed upon trivalent molybdenum solutions.

RÉSUMÉ

La préparation de l'oxinate de molybdène^{VI} et d'un complexe molybdène^{V}-oxine est décrite. Ce dernier a été analysé; un certain nombre de ses propriétés ont été étudiées, comprenant sa séparation d'avec le composé du molybdène^{VI} par chromatographie. La préparation d'une solution renfermant le molybdène^{III} et la séparation du molybdène^{III} d'avec le molybdène^{V}, par chromatographie sur cellulose, sont décrites. Des hypothèses ont été faites au sujet de la stabilité des thiocyanate et oxinate de molybdène^{III}, à partir des résultats de quelques essais d'extraction effectués avec des solutions de molybdène^{III}.

ZUSAMMENFASSUNG

Die Darstellung von Molybdän^{VI}-Oxinat und von einem Molybdän^{V}-Oxin-Komplex wird beschrieben. Dieser Letztere wurde analysiert; eine gewisse Anzahl seiner Eigenschaften wurde untersucht, unter anderen seine Abtrennung von der Molybdän^{VI}-Verbindung mittels Papierchromatographie. Die Darstellung einer Lösung, welche Molybdän^{III} enthält und die Abtrennung des Molybdän^{III} vom Molybdän^{V} mittels Zellulosechromatographie sind beschrieben. Es wurden Hypothesen aufgestellt in Bezug auf die Stabilität des Molybdän^{III}-Thiocyanats und -Oxinats, ausgehend von Resultaten einiger Extraktionsversuche, welche mit Lösungen von Molybdän^{III} ausgeführt wurden.

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ANALYSIS OF MIXTURES OF THE CONDENSED PHOSPHATES BY ION-EXCHANGE CHROMATOGRAPHY

II. MIXTURES OF ORTHO-, PYRO-, TRI-, TETRA-, TRIMETA-, AND TETRAMETAPHOSPHATES AND GRAHAM'S SALT

by

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In previous papers from this laboratory, a theoretical discussion was given of the elution behavior of polyprotic acids[1], and a method was described for the analysis of mixtures of ortho-, pyro-, tri-, trimeta-, and tetrametaphosphates[2]. In this paper, a modification of the method is described by which complete analyses may be obtained of mixtures containing the five above-mentioned phosphates plus tetraphosphate and Graham's salt.

APPARATUS AND REAGENTS

Four columns were used. Each had an internal cross-sectional area of 3.8 sq.cm and was filled to 14 cm with resin AG 1-X8, 100 to 200 mesh. Each column was provided with a water jacket connected so that the resin beds in all columns could be heated simultaneously with one circulating pump. The AG resin was obtained from Bio-Rad Laboratories, 800 Delaware Street, Berkeley, California; it is Dowex 1-X8 that has been carefully sieved and washed with acids, bases, and complexing agents. The shipment received in this laboratory was found to give narrower elution graphs and hence better separations than the resin previously[1,2] used, Dowex 1-X10, 100 to 200 mesh.

The fraction collector, pH meter, spectrophotometer, and most of the reagents have been described[1,2].

The eluant designated as $0.250M$ potassium chloride of pH 9.00 was actually $0.240M$ with potassium chloride and $0.010M$ with ammonium chloride and contained sufficient ammonia to give a pH of 9.00. Similarly, a mixture of $0.490M$ potassium chloride, $0.010M$ ammonium chloride and ammonia is designated as $0.500M$ potassium chloride of pH 9.00.

Guanidinium tetraphosphate monohydrate was prepared by the method of QUIMBY[3] except that the quantity of formamide used was 20% greater than recommended by QUIMBY. The analysis of this product is given in Table 1.

The Graham's salt was prepared by TREITLER[4], who also found its number-average degree of polymerization to be 190.

ELUTION GRAPHS

The solid graph in the upper part of Fig. 1 presents a quantitative separation of ortho-, pyro-, tri-, tetrameta-, and trimetaphosphates by elution at a flow rate of 0.6 cm per minute with three different concentrations of potassium chloride, each buffered at a pH of 5.00. The dashed line of this same figure indicates the behavior of tetraphosphate under the same elution conditions. Although the two tetramers are clearly separated from other phosphates, it is obvious that these elution conditions will not effect their separation from each other.

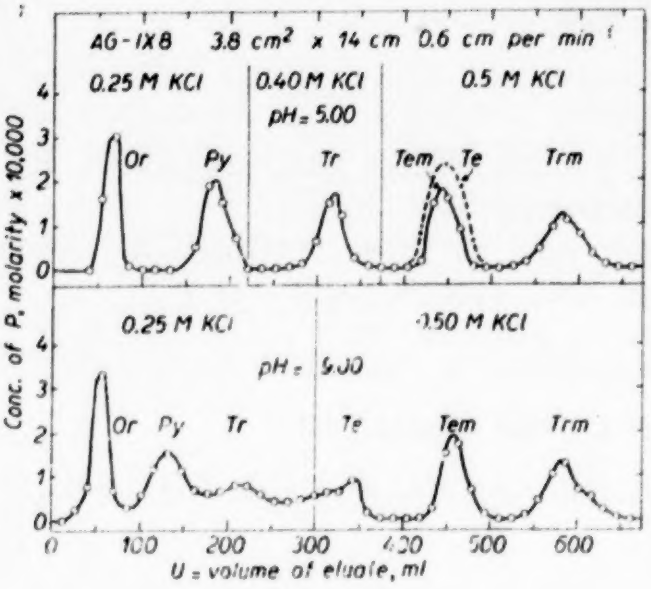

Fig. 1

The lower graph of Fig. 1 shows an elution at the same flow rate with two concentrations of potassium chloride at pH 9.00. The two cyclic phosphates are completely separated from each other and from the other phosphates under these conditions, but the ortho-, pyro-, tri-, and tetraphosphates overlap each other. Thus two elutions, one at pH 5.00 and one at pH 9.00, furnish all the data needed for the complete analysis of a mixture of the six compounds mentioned above.

If a sample containing Graham's salt is eluted at a pH of either 5.00 or 9.00 with these eluants, it remains absorbed on the upper part of the column even though several liters are passed through. However, treatment of the absorbed Graham's salt with hot 3.0*M* hydrochloric acid hydrolyzes it to lower polymers which are readily eluted from the column.

METHOD OF ANALYSIS

The sample should contain not more than 0.15 milligram atom of phosphorus in any one compound. Dissolve it in 5 ml of 0.250*M* potassium chloride buffered at pH 5.00. Add it cautiously to the resin column, previously equilibrated by the passage of 200 ml of this eluant. Drain the column at a flow rate of 0.2 cm per minute into a 250 ml graduated cylinder until the meniscus is within about 1 mm of the top of the resin. Wash the walls of the column above the resin bed with three 5-ml portions of the same 0.250*M* potassium chloride solution. After each addition of wash-solution, drain the liquid level to within 1 mm of the resin bed at a flow rate of 0.2 cm per minute.

Now elute with 220 ml of 0.250*M* potassium chloride, 150 ml of 0.400*M* potassium chloride, and 310 ml of 0.500*M* potassium chloride, each buffered at a pH of 5.00. Maintain a flow rate of 0.6 cm per minute or 2.3 ml per minute. Collect successive fractions of eluate of 110, 140, 140, 120, and 170 ml. These contain, respectively, the ortho-, pyro-, tri-, the mixture of tetra- and tetrameta-, and trimetaphosphate. Each fraction except the fourth contains only one species of phosphate.

Heat the column to 70 to 80° C by pumping hot water through the jacket. Pass 200 ml of 3.0*M* hydrochloric acid through the column at the same flow rate. Collect as the final fraction 200 ml of eluate.

Determine the phosphate content of each fraction by the depolymerization and photometric method previously described[1,2]. The last fraction must be evaporated to dryness and redissolved in water before the photometric method is applied.

Perform a similar elution simultaneously on a column previously equilibrated with 500 ml of 0.250*M* potassium chloride at pH 9.00. Use 300 ml of this eluant, 370 ml of 0.500*M* potassium chloride, and 200 ml of 3.0*M* hydrochloric acid as before. Collect fractions of eluate of 400, 120, 150, and 200 ml. These contain, respectively, the mixture of orthophosphate with the first three linear polymers, the tetrameta-, the trimetaphosphate and the depolymerized Graham's salt.

If calculation method A (see below) is to be applied, it is necessary to determine only the tetrametaphosphate in the second fraction, although the analyst may wish to determine also the trimetaphosphate in the third fraction and the depolymerized Graham's salt in the fourth fraction as checks on the elution at pH 5.00.

If means are not available for heating the columns, equally good results can be obtained in the following manner. Pass 50 ml of 3.0*M* hydrochloric acid through the column at room temperature. Let the column stand overnight in contact with the acid. Then pass an additional 175 ml of 3.0*M* hydrochloric acid through the column. In this case, the last fraction will have a volume of 225 ml.

Calculations

If the phosphorus found in the second fraction of eluate of pH 9.00 is subtracted from the phosphorus found in the fourth fraction of the eluate of pH 5.00, the difference is the amount of phosphorus present in the sample as tetraphosphate. This is designated as Method A.

If the sum of the phosphorus found in the elution at pH 5.00 as ortho-, pyro-, and triphosphate is subtracted from the phosphorus found in the first fraction of the eluate of pH 9.00, the difference is the phosphorus present in the sample as tetraphosphate. This is designated as Method B.

It is assumed in the foregoing statements that exactly the same weights of sample were taken in both elutions. If this is not the case, the quantities of phosphate found in the elution at pH 9.00 should be proportionately corrected on the basis of the sample weight taken for the elution at pH 5.00.

RESULTS

In order to test the purity of the individual phosphates used in this investigation, samples of each of the seven phosphates were subjected to the foregoing analytical methods. The results are listed in Table I. Each entry is the mean of three determinations. The maximum value of the absolute mean deviation is 1.3%; and the average value, exclusive of those with 0.0 percentage, is 0.6%. All results except those for the guanidinium tetraphosphate and Graham's salt were calculated on a dry basis.

TABLE I

ANALYSIS OF INDIVIDUAL PHOSPHATES

Phosphate			*Percent of total P present as*				
Taken	*Ortho*	*Pyro*	*Tri*	*Tetra*	*Tetrameta*	*Trimeta*	*Graham's Salt*
K_2HPO_4	99.9	0.0	0.0	0.0	0.0	0.0	0.0
$Na_4P_2O_7$	3.6	95.7	1.7	0.0	0.0	0.0	0.0
$Na_5P_3O_{10}$	1.7	5.0	88.8	0.6	0.3	0.0	2.9
$(GuH)_6P_4O_{13}$	4.2	1.6	2.9	79.9	0.0	0.0	0.0
$Na_4P_4O_{12}$	1.2	0.5	1.5	1.6	95.2	0.6	0.0
$Na_3P_3O_9$	3.0	1.6	0.0	0.0	0.0	95.3	0.0
$(NaPO_3)_n$	0.0	0.0	0.0	0.0	3.1	3.9	91.4

As a test of the accuracy of the method, mixtures containing known quantities of each of the phosphates were prepared and submitted to analysis. These results are shown in Table II. Each entry under the headings "Found" is the mean of two independant determinations. For hexaguanidinium tetraphosphate, two results are given — the first obtained by Method A, the second by Method B of the calculations. It is seen that results of very satisfactory accuracy are obtained by both methods of calculation.

TABLE II

ANALYSIS OF PHOSPHATE MIXTURES

	Mixture 1 90.9 mg		*Mixture 2* 69.6 mg		*Mixture 3* 70.1 mg	
Phosphate	*Taken* %	*Found* %	*Taken* %	*Found* %	*Taken* %	*Found* %
K_2HPO_4	22.0	22.2	29.3	29.2	12.4	12.4
$Na_4P_2O_7$	14.5	14.4	7.8	7.9	20.0	19.9
$Na_5P_3O_{10}$	12.7	12.6	16.8	16.7	7.0	6.8
$(GuH)_6P_4O_{13}$	21.9	A 22.0 B 21.7	12.4	A 12.2 B 11.9	31.2	A 30.8 B 31.5
$Na_4P_4O_{12}$	9.9	10.0	14.9	14.7	9.1	9.1
$Na_3P_3O_9$	9.2	9.1	5.3	5.3	14.7	14.8
$(NaPO_3)_n$	9.8	9.7	13.5	13.5	5.6	5.5

DISCUSSION

If four elutions, two at each pH, are performed simultaneously, a duplicate analysis can be completed in 8 hours. The attention of the operator is required for much less than half of this time.

Recently, two papers have been published that report the analysis of mixtures of condensed phosphates by paper chromatography. GERRITSMA AND FREDERIKS[5] have determined ortho-, pyro-, tri-, and trimetaphosphates and Graham's salt in mixtures. WESTMAN AND CROWTHER[6,7] have used paper chromatography to determine phosphorus compounds up to nonaphosphate. The results for the lower members (including tetraphosphate) were accurate to ± 0.8% of the total phosphorus. Results for penta-, hexa-, septa-, octa-, and nonaphosphate were precise to ± 2% of the total phosphorus. Molecules that contained more than nine phosphorus atoms were reported as "high polymers." Thus it is seen that paper chromatography has at present succeeded in isolating more members of the series of polyphosphates than ion-exchange chromatography. The latter technique, however, requires much less time and yields more accurate results.

HIGGINS AND BALDWIN[8] have used ion-exchange chromatography to analyse mixtures of orthophosphoric acid with its linear polymers as high as pentaphosphoric acid. They used unbuffered eluants. The duration of their elutions was 14 hours. The precision of their method seems to be about the same that as of the method described in this paper.

U. P. STRAUSS AND T. L. TREITLER of this laboratory are studying the kinetics of the depolymerization of Graham's salt in aqueous solution. In the course of this investigation, they analyse partially degraded Graham's salt by the method described in this paper. Anomalous results are obtained with samples of extensively depolymerized Graham's salt. It is believed that pentaphosphate is present in these extensively degraded samples and interferes in the analytical procedure by appearing with trimetaphosphate at pH 5.00 and with tetrametaphosphate at pH 9.00. Work is being continued to develop analytical methods for the analysis of phosphate mixtures containing pentaphosphate and higher polymers.

The theoretical principles of ion-exchange chromatography, previously discussed[1], were used to develop the methods of analysis described in this paper. Although the exchange constants and ionization constants of tetraphosphoric acid were not evaluated, the elution characteristics of this compound could be predicted with fair accuracy by extrapolation of the series, ortho-, pyro-, and triphosphoric acids.

It is well known that commercial ion-exchange resins differ slightly from batch to batch. Therefore, a different batch of Dowex 1-X8 may require slightly different elution conditions to yield quantitative separations such as those described in this paper.

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SUMMARY

When a mixture of condensed phosphates is eluted on a column of Dowex-1 with various concentrations of potassium chloride buffered at pH 5.00, appropriate fractions of the eluate contain (1) orthophosphate, (2) pyrophosphate, (3) triphosphate, (4) a mixture of tetra- and tetrametaphosphates, and (5) trimetaphosphate. A similar elution with eluants buffered at pH 9.00 yields eluate fractions containing (1) a mixture of ortho-, pyro-, tri-, and tetraphosphates, (2) tetrametaphosphate, and (3) trimetaphosphate. In both elutions, Graham's salt is retained on the column until it is treated with hydrochloric acid. Thus two elutions serve for the determination of the seven constituents.

RÉSUMÉ

Lorsqu'on rince un mélange de phosphates condensés, sur une colonne de Dowex-1, avec des solutions de chlorure de potassium, à diverses concentrations, à pH 5.00, on obtient les fractions d'éluat suivantes: (1) orthophosphate, (2) pyrophosphate, (3) triphosphate, (4) mélange de tétra- et tétramétaphosphates et (5) trimétaphosphate. Une élution similaire avec des solutions éluantes à pH 9.00 donne des fractions d'éluat contenant: (1) mélange d'ortho-, de pyro-, de tri- et tétraphosphates, (2) tétramétaphosphate, et (3) trimétaphosphate. Dans ces deux élutions, le sel de Graham reste dans la colonne; il est traité ensuite par l'acide chlorhydrique. Deux élutions suffisent donc pour le dosage des sept constituants.

ZUSAMMENFASSUNG

Man eluiert ein Gemisch von kondensierten Phosphaten aus einer Säule von Dowex-1 mit Kaliumchloridlösungen von verschiedenen Konzentrationen bei pH 5.00. Geeignete Teile des Eluats enthalten dann (1) Orthophosphat, (2) Pyrophosphat, (3) Triphosphat, (4) eine Mischung von Tetra- und Tetrametaphosphaten, und (5) Trimetaphosphat. Eine ähnliche Elution bei pH 9.00 gibt Teile des Eluats, die (1) eine Mischung von Ortho-, Pyro-, Tri-, und Tetraphosphaten, (2) Tetrametaphosphat, und (3) Trimetaphosphat enthalten. In beiden Elutionen bleibt das Graham'sche Salz am Harz bis man es mit Salzsäure behandelt. Man erzielt also eine Bestimmung aller sieben Phosphatarten durch zwei Elutionen.

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APPLICATION OF VAPOUR PHASE CHROMATOGRAPHY IN THE GAS-ANALYTICAL FIELD

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INTRODUCTION

Chromatography in its various forms has found an extremely wide application in laboratory science and in industry.

The analysis of mixtures of components in the gas or vapour phase represents one of the most recent applications in chromatography. The techniques employed for this purpose — which are generally known collectively as vapour phase chromatography — have rapidly become of great importance in the analytical field owing to their rapidity, selectivity and ease of execution with automatic recording equipment.

Vapour phase chromatographical methods may be subdivided into two groups:
(a) those employing a solid adsorbing agent (gas-solid chromatography);
(b) those using a liquid agent for partition (gas-liquid chromatography).

Gas-solid chromatography may again be carried out in two forms. The methods first employed were based on separation by displacement. The gaseous mixture is adsorbed onto activated charcoal or silica gel in a column and subsequently desorbed selectively by a gradual increase in temperature[10,20], or else it is displaced by a vapour that is more powerfully adsorbed[3,9].

In the second method of gas-solid chromatography (gas-solid elution chromatography) the adsorbed components are eluted by means of an inert stripper gas. The latest developments in this field have been described by JANAK[13], PATTON[18] and RAY[19]. The great forces with which the components are bound to solid adsorbents allow the low molecular weight gases, such as hydrogen, nitrogen, rare gases, methane, ethane and propane, to be separated. For the separation of the high molecular weight compounds, however, the strong adsorption is a drawback. A corresponding increase in column temperature to weaken these forces of adsorption gives rise to the risk of chemical reactions. Complete desorption may be realized by displacement with a vapour of greater adsorbability, but each analysis requires a fresh charge in the column[4,8]. Furthermore, the possibilities of the gas-solid elution technique are limited by the small number of suitable adsorbents, as well as by the considerable influence of their quality and of the pretreatment they have undergone on the sharpness of separation.

Gas-liquid partition chromatography proves to be much more attractive for the analysis of hydrocarbon gases. In 1952 MARTIN and co-workers[11,12] gave a detailed description of the separation of volatile compounds according to this principle.

The procedure is as follows. The chromatographic column is charged with a non-volatile absorption liquid (the stationary phase) on an inert solid carrier and the volatile mixture to be separated is eluted from the column with the aid of an inert stripper gas. The components of the mixture pass through the column at a velocity proportional to their respective Henry-coefficients and their concentrations in the stripper gas can be measured at the outlet of the column. If the non-volatile absorption liquid is stable, the contents of the column may be used for an unlimited number of runs.

Obviously, the fact that there is a wide range of suitable absorption liquids of greatly varying selective properties renders this technique much more flexible than gas-solid chromatography; the liquid phase can be selected in accordance with the separation problem in question. Several of these absorption liquids are discussed in detail by KEULEMANS and co-workers[14].

Applications of this analytical separation technique to gas mixtures have been described by RAY[19] and BRADFORD[1].

The present paper discusses a few aspects of the separation of hydrocarbon gases (C_1–C_5) and the quantitative determination of the components in more detail.

EQUIPMENT

Fig. 1 shows the principle of the apparatus employed for the form of analysis to be described first. It is provided with a device for measuring thermal conductivity. A gas sample of known volume is introduced by the stripper gas into the column, where it is subjected to separation; the changes in concentration of each component in the gas leaving the column are recorded by means of thermal conductivity measurement. Figs. 2-5 give a few examples of the type of chromatogram obtained in this way.

SEPARATION

The quantitative analysis of a mixture in the first place requires an effective separation of the components. The theory of gas-liquid partition chromatography which was developed by MARTIN[12] and others gives some guiding principles that are of importance for the separation, but owing to the large number of factors playing a part in the process it is not yet possible to predict the optimum conditions for each problem.

The main factors of importance for separation are:

(a) factors determining the Henry-coefficient:
 the nature of the absorption liquid and the column temperature;
(b) the other operational variables:
 the dimensions of the column, the size of sample, the type of carrier, and the velocity of the stripper gas.

(a) The nature of the absorption liquid and the temperature determine the relative volatility of the components to be separated in the column. The retention volumes of the components, or the retention times at a given velocity of the stripper gas, are inversely proportional to the respective Henry-coefficients of these components.

An effective analytical separation can be realized if the ratio of the retention volumes of two components is higher than 1.10.

Theoretically a low temperature promotes the separation, but fortunately this influence is not a critical one and mixtures with a boiling range of 50 or even 100° C can be analysed at a single column temperature. By a suitable choice of the other conditions (*e.g.* the column length), hydrocarbon gas mixtures both in the methane-ethane range and in the butane-pentane range can be separated at a temperature of +30° C. Thus, the apparatus retains its simple and flexible character.

The choice of the liquid phase is determined by the nature of the compounds to be separated. If a non-polar liquid (*e.g.* "liquid paraffin") is used, the hydrocarbons are separated virtually according to boiling point. Hence this type of immobile phase gives an easy separation of the saturated hydrocarbon gases C_1 to C_5, but not, say, of mixture of 1,3-butadiene (b.pt. —4.4° C), *iso*-butene (—6.9° C) and 1-butene (—6.3° C).

The solubility of olefins in polar liquids is considerably greater than that of the corresponding paraffins. If the liquid phase consists of dimethyl sulpholane (b.pt. 280° C), for instance, propene (b.pt. —48° C) and propane (b.pt. —42° C) leave the column in reverse order, the retention time of the propane being shorter than that of propene.

Dimethyl sulpholane cannot, however, effect the complete separation of *iso*-butene and 1-butene*. Dimethyl formamide (b.pt. 155° C) can be used for this purpose (see Fig. 5), but has the drawback that at 0° C the vapour tension is still 0.8 mm, so that the separating power of the column gradually decreases owing to loss of the immobile phase. For quantitative work this is a disadvantage.

BRADFORD[1] has pointed out that it is possible to separate olefins by using a glycolic solution of $AgNO_3$ as the liquid phase. This may be explained by the fact that these olefins form unstable complexes[6] with $AgNO_3$. The unsaturated C_4 hydrocarbons are separated in the order: *trans*-2-butene (b.pt. +0.9° C), *iso*-butene (—6.9° C), *cis*-2-butene (+3.7° C), 1-butene (—6.3° C), 1,3-butadiene (—4.4° C). The butanes do not form complexes and pass through the column very quickly without being separated. As glycols are very hygroscopic the stripper gas and the samples must be perfectly dry in order to keep the separating power of the column constant. It was found that for this reason a saturated solution of $AgNO_3$ in benzyl cyanide is preferable to a similar solution in glycol.

An important tool for the separation of complex gas mixtures is a system of two columns with different liquid phases. By placing these in series and choosing suitable lengths it is often possible to separate one component from those which would cause interference if each of the columns were used separately. This point will be further discussed when dealing with the examples.

(b) If the concentrations of the components in the stripper gas are plotted against time (volume of stripper gas), a chromatogram as shown in Figs. 2-5 is obtained. The ratios of the retention times of the components are exclusively determined by the nature of the liquid phase and the temperature of the column. If, however, substances differing little in volatility have to be separated, the peak widths are very important for quantitative analysis. It is mainly the diffusion phenomena occurring in the column, which determine the width of a peak.

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* FREDERICKS AND BROOKS[17], however, succeeded in getting sufficient separation for analytical use, but only by using columns of 15 m length (private communication).

For the vapour-liquid equilibrium to be established rapidly the liquid must be deposited on the inert solid carrier in a very thin layer. Most investigators have used Celite 545 (grain size 20–40 μ) as carrier with about 30%w of liquid. It has been found that a smaller quantity of liquid (15-25%w) often improves the separation. At the same time, this has the advantage of reducing the time required for analysis; the retention volumes are directly proportional to the quantity of liquid phase in a column. The viscosity of the liquid phase also plays a rôle in equilibration. The choice is limited, however, as the requirements of polarity and low volatility must also be satisfied.

The velocity of the gas is not a very critical factor, although at high and low velocities the peaks tend to become wider on account of both back diffusion and incomplete equilibration. For 6 mm diameter columns with Celite as the carrier these "critical" values are approximately ½ and 5 l/h respectively. At gas velocities higher than 3 l/h, however, columns charged with Celite are unsuitable, as their resistance is high (*ca.* 0.4 atm per 2 m of length at 3 l/h). Therefore a search was instituted for a carrier material with a lower resistance, which would make it possible to use longer columns for difficult separations without the need of more time for the analysis.

Certain screen fractions of ground insulating bricks[15] (*e.g.* Sterchamol*) as carriers give complete satisfaction. The resistance of this material at a grain size of 50-80 mesh (0.2-0.3 mm) is a third of that of Celite, but the separations effected are practically equivalent. At larger grain sizes (30-50 mesh = 0.3-0.6 mm) the efficiency of separation is slightly reduced. Sterchamol need not be subjected to a special pretreatment, except for removal of dust by suspension in water and drying at 150° C. The liquid phase can be deposited by diluting it with a volatile solvent (say 1 to 5), mixing it with the carrier and evaporating the solvent with continuous stirring. Besides the low resistance, the fact that the method of filling the columns is simple and shows better reproducibility, provides an important advantage of Sterchamol over Celite. As this new carrier material permits the use of columns with a length of 6 m, the separation of CH_4, C_2H_2, C_2H_4 and C_2H_6 no longer presents any difficulties.

In actual practice use is made of column sections of 2 m length, which are interconnected as and when required. Copper columns, after having been filled, can be coiled in order to save space.

Experiments carried out with columns of different diameters varying from 4 to 14 mm have shown that the separation efficiency is independent of the column diameter so long as the size of the sample is varied in proportion and the linear gas velocity remains the same. Within these limits no disturbing radial diffusion apparently occurs. Hence the column diameter can be adapted to the measuring system used for the determination of the components.

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* Sterchamol is a proprietary brand of refractory brick.

For a separation in a given column and with otherwise identical experimental conditions, there is an advantage in reducing the size of the samples. In quantitative analysis the lower limit is determined by the sensitivity of the measuring system. In columns with a diameter of 6 mm we use gas samples of 1-20 ml (NTP), according to the desired separation or the accuracy with which traces have to be determined.

QUANTITATIVE ANALYSIS

Two methods have been used for detecting and measuring the components separated in the column:

1. continuous measurement of the concentration of the components in the stripper gas leaving the column, on the basis of differences in thermal conductivity (indirect determination);
2. Determination of the absolute quantity of each component by volume or pressure measurement, after removal of the stripper gas (direct determination).

Re 1.

Various methods, based on the measurement of a physical quantity, can be used for an indirect determination. In their publications GRIFFITH[8] and HAMMAR[9] give many references on the subject.

Of all these methods we chose thermal conductivity, as it combines sensitivity with comparative simplicity, and no difficulties are encountered in recording.

The thermal conductivity cell used in this laboratory is of the Bureau of Mines type, as described by PALMER AND WEAVER[17]. It consists of a copper block pierced by two parallel channels 10 cm in length and 3 mm in diameter, in which platinum wires 0.02 mm in diameter are stretched. The gas mixture flows through one channel, the stripper gas used as reference through the other. The platinum wires are connected to a source of electricity and form two arms of a Wheatstone bridge. The out-of-balance voltage of the bridge, caused by the different resistance of the two wires due to differences in heat conduction, is recorded by means of a 0-2½ mV Brown pen recorder. The cell is placed in the same air thermostat as the sample inlet system and the columns and is maintained at a temperature of 30 ± 0.2° C.

The changes in concentration of the components in the stripper gas leaving the column are thus measured continuously, so as to yield a chromatogram of a differential type as shown in Figs. 2-5.

The area of a peak is proportional to the quantity of the component in question if the gas velocity is constant and the deflection of the thermal conductivity device is directly proportional to the concentration of that component in the stripper gas. This frequently is the case for concentration up to 10%.

Instead of measuring the actual peak area it is usually sufficient to determine it approximately, for instance by multiplying the peak height by the width halfway up[5], or by drawing the tangents to the peak and multiplying the width at the base thus obtained by the height. As the various gases differ greatly in thermal conductivity the relation between peak area and quantity of component must be determined with the aid of pure substances or synthetic gas mixtures.

Peak heights are easier to determine than peak areas, but the measurement of peak heights requires a greater constancy of separating conditions. A change, *e.g.* of temperature or column charge, results in a different *shape* of the peak, the peak *area* remaining the same. Quantitative analysis based on peak height measurements is consequently only used for the determination of low concentrations of a component (< 10%) in products whose main composition varies little; this restriction is also necessary owing to the fact that the shape of the peak for a given component is not entirely independent of the other components in the mixture analysed.

The latter influence makes itself felt chiefly in the first part of the column and might be explained as follows. As the heaviest component dissolves in the stationary phase, the concentration of lighter components in the gas increase, with the result that the concentration at which the latter dissolve is also higher. Consequently the peak height of the light component increases, the base becoming narrower. The influence of light components on the peak shape of the heaviest components is small. Tables I and II record the results of a series of measurements on mixtures of various compositions.

TABLE I

INFLUENCE OF COMPOSITION OF SAMPLE ON PEAK HEIGHT OF A COMPONENT

Column	: length 200 cm; diam. 7 mm; liquid phase: C_{19}-paraffins on Sterchamol
Stripper gas	: nitrogen, 2 l/h
Size of sample	: 10 ml

Percentage of component in sample	*Peak height for 1% of component*										
	C_2H_6 in				*C_2H_4 in*	*C_3H_8 in*			*n-C_4H_{10} in*		
	N_2	*C_2H_4*	*C_3H_8*	*C_4H_{10}*	*C_2H_6*	*N_2*	*C_2H_6*	*C_4H_{10}*	*N_2*	*C_2H_6*	*C_3H_8*
5	3.25	—	4.64	4.28	—	5.84	5.75	6.27	4.22	4.30	4.16
10	3.23	4.15	4.18	3.88	5.66	5.48	5.36	5.73	3.98	4.00	3.91
50	2.24	—	2.51	2.20	—	3.11	3.01	3.46	2.61	2.72	2.61
90	1.71	1.69	1.70	1.71	2.73	2.48	2.49	2.48	2.04	2.01	2.05
95	1.66	—	1.66	1.67	—	2.41	2.42	2.43	1.98	2.00	1.98
100	1.64	—	1.64	1.64	—	2.36	2.36	2.36	1.98	1.98	1.98

TABLE II

INFLUENCE OF COMPOSITION OF SAMPLE ON PEAK AREA OF A COMPONENT

Percentage of component in sample	*Peak area for 1% of component*										
	C_2H_6 in				*C_2H_4 in*	*C_3H_8 in*			*n-C_4H_{10} in*		
	N_2	*C_2H_4*	*C_3H_8*	*C_4H_{10}*	*C_2H_6*	*N_2*	*C_2H_6*	*C_4H_{10}*	*N_2*	*C_2H_6*	*C_3H_8*
5	19.2	—	19.5	20.2	—	53.7	54.8	56.3	89.8	90.1	90.0
10	19.7	20.0	20.1	19.5	56.6	53.8	54.7	56.2	87.8	89.8	89.7
50	19.9	—	20.3	20.9	—	56.0	54.5	56.2	89.0	89.2	89.4
90	20.4	20.1	19.6	19.2	59.5	55.5	55.9	54.5	89.5	89.7	89.7
95	20.3	—	20.0	20.6	—	56.0	55.1	56.4	87.7	88.5	89.7
100	20.5	—	20.5	20.5	—	55.9	53.8	56.7	90.0	90.0	90.5
Mean	20.0	20.0	20.0	20.1	58.0	55.2	54.8	56.0	89.0	89.6	89.8

The fact that the components do not affect each other over the whole length of the column is apparent from the following experiments, which were carried out in columns of various lengths.

TABLE III

INFLUENCE OF COLUMN LENGTH ON THE SHAPE OF THE PEAK OF A COMPONENT IN TWO DIFFERENT MIXTURES

Length of column, cm	*Peak height for 1 % of component*			*Peak area for 1 % of component*	
	10% C_2H_6 in			*10% C_2H_6 in*	
	N_2	*C_3H_8*	*Difference*	*N_2*	*C_3H_8*
200	3.23	4.18	29%	19.7	20.1
400	2.48	2.85	15%	20.3	19.9
600	2.04	2.15	5%	19.8	19.6

The percentage differences between peak heights for C_2H_6 in mixtures with N_2 or with C_3H_8 are 29% in the 2 m column and only 5% in the 6 m column.

The peak areas as determined by the method of tangents are practically independent of the length of the column and of the other components, as is apparent from Tables II and III.

If the peak height is taken as a measure of the content of a component, calibration should be carried out with synthetic mixtures whose composition is about the same as that of the gases to be analysed.

Area measurement is suitable for analysing mixtures whose composition is in sufficiently known. In this case calibration is simpler because, unlike peak height, the area increases proportionally with the content.

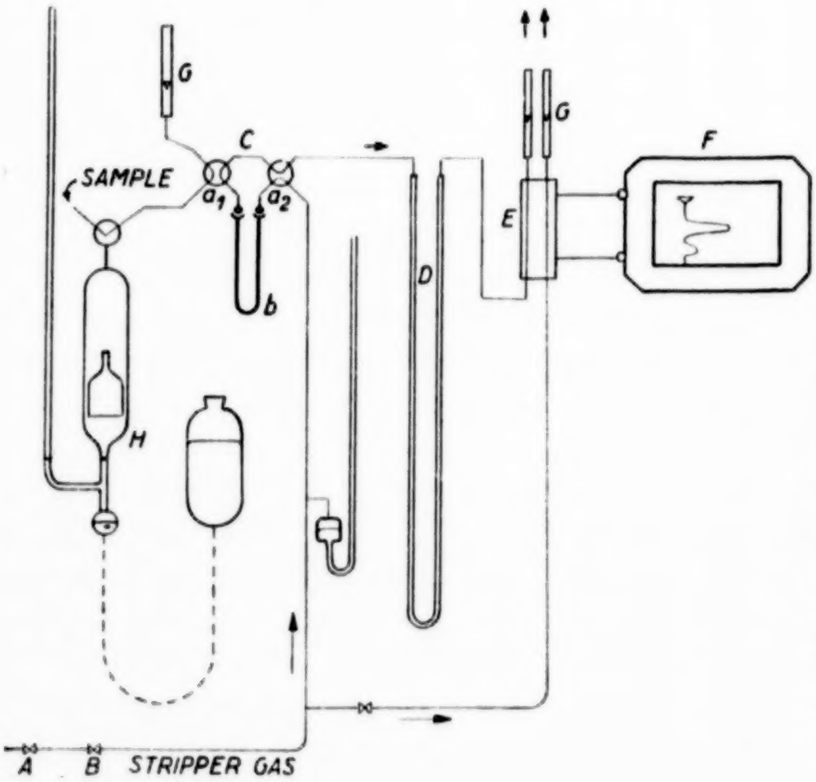


Fig. 1. Gas analysis apparatus with thermal conductivity recording.

A. Technical reducing valve
B. Precision reducing valve
C. Sample inlet system
a_1 a_2 Four-way cocks
b. Sample tube
D. Separating column
E. Thermal conductivity cell
F. mV Recorder
G. Rotameters
H. System for preparing calibration mixtures

For the accuracy of the method it is of paramount importance that gas samples of constant volume should be introduced into the column in a reproducible way. The best results were obtained with the device shown in Fig. 1, in which a given volume of gas is confined between two four-way cocks and, on opening one of these, is entrained by the stripper gas. By measuring the gas sample at barometric pressure and keeping the pressure in the thermal conductivity cell equal to atmospheric, variations in barometric pressure are automatically corrected. The stop cocks must be lubricated with a hydrocarbon-insoluble lubricant. A mixture of starch, mannitol and glycerol[2] is excellent; products such as vaseline and silicones are entirely unsuitable.

A value of general validity for the accuracy of this form of gas analysis cannot be given, as it is dependent on many factors differing for each type of gas mixture. With the apparatus described, the method of peak height measurement yields more accurate results than that of area measurement if a stable stationary phase, for instance, a non-volatile liquid paraffin, is used. In this case calibrations for peak heights are very nearly constant and components that are completely separated from the remainder can be determined to within about 2% of the actual percentage, with a lower limit of about 0.05% absolute, *i.e.* the content is determined as 50.0 ± 1.0% mol, 10.0 ± 0.2% mol, or 1.00 ± 0.05% mol.

Area measurements have to be employed when the calibration cannot be carried out on mixtures of corresponding composition, or when the stationary phase is not sufficiently stable.

Peak area measurements, however, show a greater spread than peak height measurements, because measuring the length of the base introduces additional errors. The deviations in analytical results are at least twice as large as those based on peak height measurements.

The maximum accuracy is ultimately determined by the accuracy with which the calibration mixtures can be composed.

The sensitivity of the thermal conductivity measurement can, moreover, be influenced by the nature of the stripper gas. The difference in conductivity, for instance, between the C_2 hydrocarbons and N_2 is only small, so that CO_2 is preferable as stripper gas. On the other hand, CO_2 is not very suitable for the analysis of C_4 and C_5 hydrocarbons. By using the correct stripper gas it is possible to detect contents of 0.1% of each of the C_1-C_5 hydrocarbons in gas samples of 5-10 ml.

TABLE IV

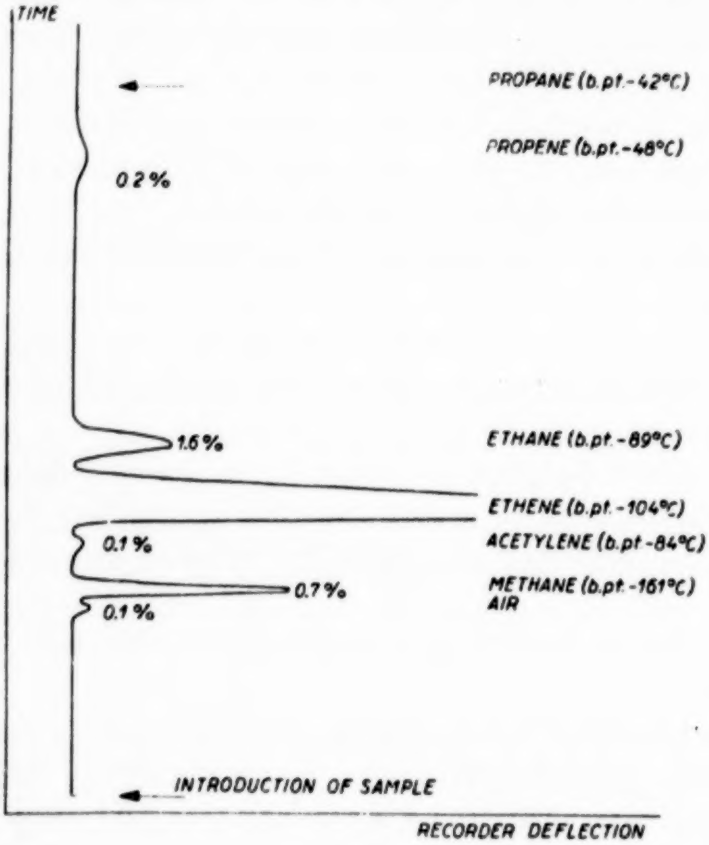
ANALYSES OF GAS MIXTURES WITH THE AID OF VARIOUS STATIONARY LIQUIDS

Sample	*Ethene*	*Propane-Propene*			*Butane-Butene*
Figure	2	3	4		5
Size of sample, ml	5	5	2		5
Chrom. column:					
length, m	6	2	1 +	5	4
diameter, mm	6	6	6	6	6
temperature, °C	+30	+30	+30	+30	0
Stationary liquid	liquid paraffin	liquid paraffin	liquid paraffin	dimethyl sulpholane	dimethyl formamide
Conc. of st. liq. on					
support, %w	30	15	15	25	25
stripper gas	CO_2, 3 l/h	N_2, 3 l/h	N_2, 3 l/h		N_2, 3 l/h
Time of analysis, minutes	12	8	20		20

The advantages of the thermal conductivity method are that:

1. the required measuring and recording equipment is fairly simple, and
2. after use the apparatus is immediately ready for the next analysis.

The method has the drawback that each thermal conductivity cell must be calibrated for all components under the conditions (temperature, gas velocity) at which it will be used. Examples of the type of gas mixtures that can be analysed with the aid of thermal conductivity measurements are given in Table IV and Figs. 2-5.



Liquid paraffin (transformer oil, b.pt. *ca.* 300° C) is a suitable liquid phase for the determination of the contaminations in ethene (Fig. 2). As the solubility of the low molecular weight components at 30° C is only small, 30% of liquid paraffin is deposited on the carrier (Sterchamol, 50-80 mesh) and a 6-metre column is used.

Fig. 2. Analysis of technical ethene with liquid paraffin as the stationary liquid.

Liquid paraffin is also very suitable for the determination of high and low boiling components in propane and propene (Fig. 3). The components are separated according to boiling point. If the product contains large quantities of propane and propene they are separated only to a very slight extent.

The determination of C_3 and C_5 hydrocarbons in a butane-butene product can be done in the same way. The analysis takes about 20 minutes (up to and including 2-methyl-2-butene) if the stripper gas has a flow rate of 5 l/h.

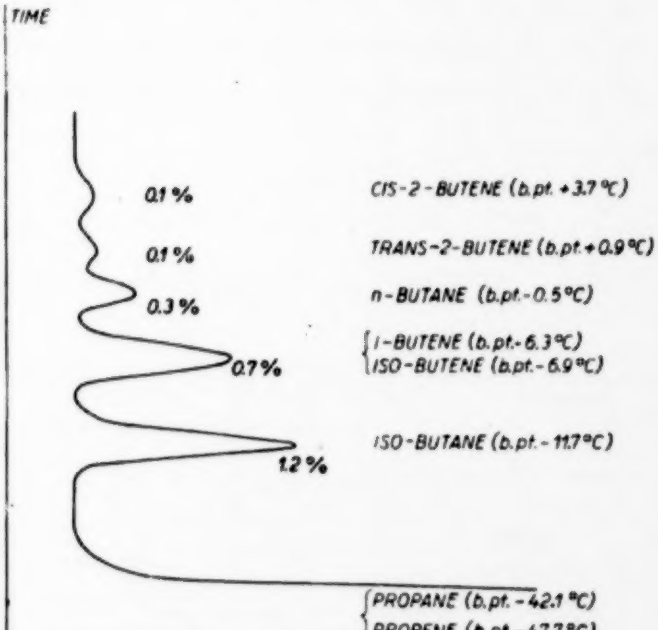


Fig. 3. Determination of low and high-boiling components in technical propane.

Propane and propene can be separated with dimethyl sulpholane, but *iso*-butane has the same retention time as propene and thus causes interference. If, however, a column containing dimethyl sulpholane is combined with one containing liquid paraffin, the latter effects a separation according to boiling point and the determination of propene is no longer disturbed by the *iso*-butane (Fig. 4).

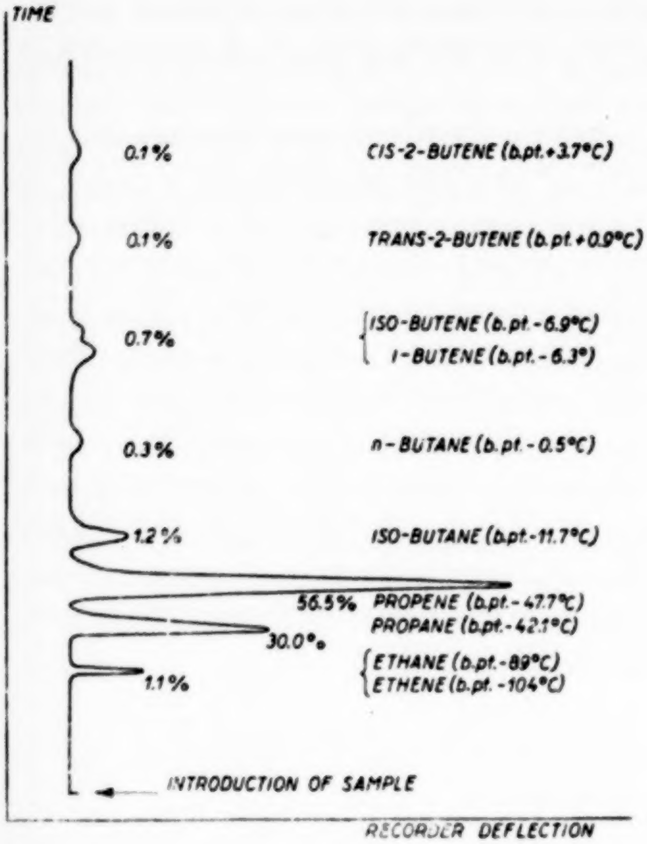


Fig. 4. Analysis of a propane-propene mixture with dimethyl sulpholane as the stationary liquid.

Iso-butene and 1-butene cannot be separated with liquid paraffin and only partially with dimethyl sulpholane. By the use of a strongly polar liquid, such as dimethyl formamide (Fig. 5), the separation of the components can be achieved; 1-butene leaves the column before *iso*-butene, notwithstanding the fact that its boiling point is somewhat higher.

Re 2.

Quantitative analysis by direct measurement of the quantity of a component after removal of the stripper gas has the advantage that no calibration with gas mixtures of known composition is required.

Even if a complete chromatographic separation is not effected, a direct measure of the total quantity of each fraction is obtained, which is not the case if the thermal conductivity method is employed. The temperature of the column and the rate of stripping need not be constant; they can, if necessary, be changed during analysis so as to obtain optimum separations in a minimum of time.

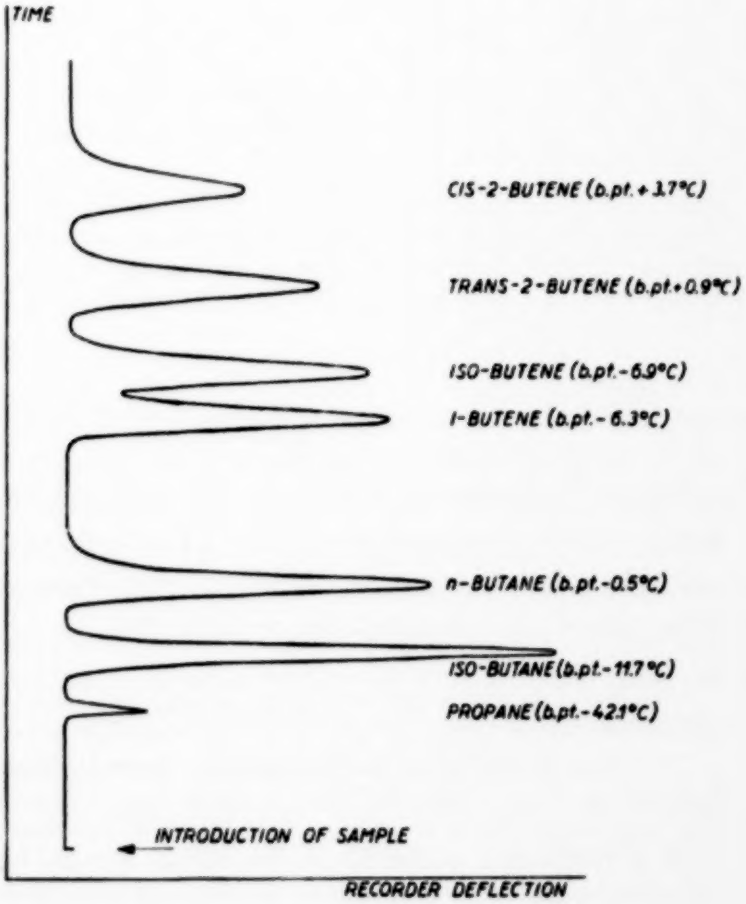


Fig. 5. Analysis of a butane-butene mixture, with dimethyl formamide as the stationary liquid.

Carbon dioxide, a gas that can be absorbed in alkaline solutions without undergoing disturbing reactions with hydrocarbons, is practically the only suitable stripper gas for this method.

The quantities of gas can be determined in two ways, *viz.* by measuring either the gas volumes at constant pressure or the increments in pressure occurring in a vessel of constant volume. The simplest method is volume measurement in a nitrometer filled with a KOH solution, a method which Janak[13] and others have followed in gas-solid chromatography. For the determination of low molecular weight gases (permanent gases and hydrocarbons up to propane) this method of measurement gives excellent results. The analysis of gas mixtures containing higher molecular weight compounds is affected by inaccuracies due to the fact that, for instance, butenes dissolve in the relatively large quantity of absorption liquid. CO_2 absorption in a separate small scrubber under reduced pressure improves the accuracy and makes it possible also to determine the components condensing at normal pressure. As, however, volume measurement cannot be combined with automatic recording in a simple way it has been replaced by pressure measurement.

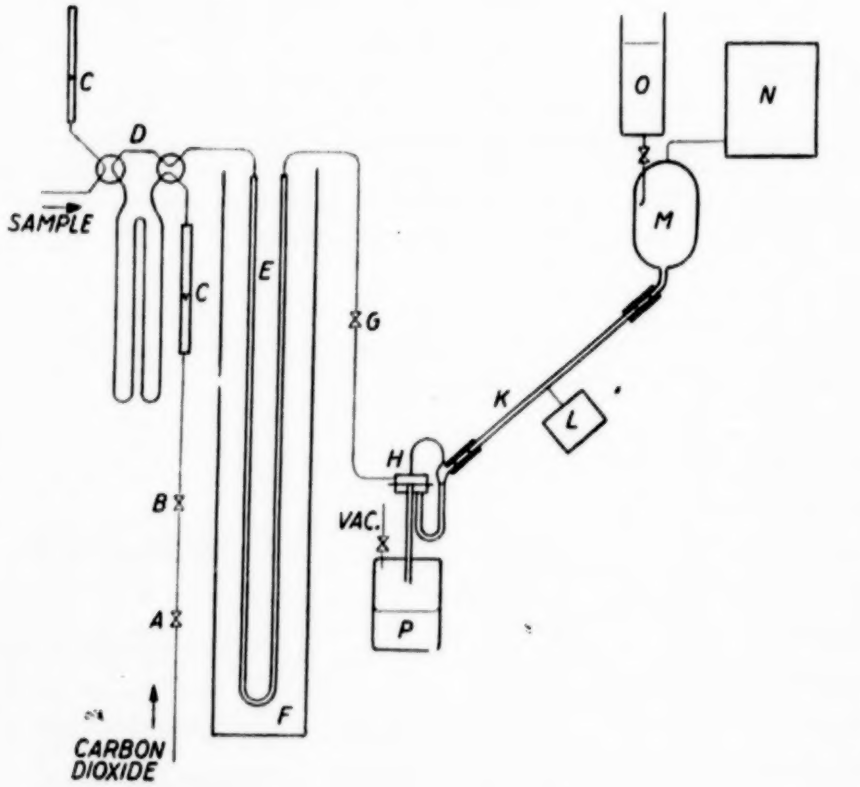


Fig. 6. Gas analysis apparatus with pressure recording

A. Technical reducing valve
B. Precision reducing valve
C. Rotameters
D. Sample inlet system
E. Separating column
F. Heating bath
G. Release valve
H. Level controller
K. CO_2 scrubber
L. Vibrator
M. Receiving vessel
N. Recording manometer
O. KOH-Solution
P. Spent caustic

Fig. 6 gives the principle of the apparatus developed for this method of measurement. After absorption of the CO_2 the components or fractions separated in the column are collected in an evacuated vessel and the increments in the pressure in this vessel are electrically recorded.

The manometer is an electromagnetic precision meter of the type described by Kinkel[16]. Over the range of 0-300 mm Hg the linearity is better than 0.1% of the full measuring range.

The absorption liquid (KOH, 50%w) flows to the absorber through the receiver and is removed through a level controller which functions independently of the gas pressure in the absorber. The requirements to be met by the absorber are that (a) complete absorption of the CO_2 is effected with a minimum quantity of absorbent, (b) no measurable back pressure occurs, and (c) its volume is small with respect to that of the receiver.

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Good results have been obtained with a stainless steel tube of 50 cm length and 5 mm diameter, which is kept in vibration by an electromagnetic vibrator. The tube contains a loosely wound coil to prevent the KOH solution from flowing off too rapidly. At a pressure of 80 mm Hg a CO_2 stream of 6 l/h (atm) is still quantitatively absorbed, notwithstanding the fact that in this case the gas, on entering the absorber, has a linear velocity of *ca.* 80 cm/sec. The KOH solution, which flows at a rate of 2 ml/min, reaches a temperature of *ca.* 60° C on the outlet side, so that its solvent power for the hydrocarbon gases is nil.

The separation of 100 ml of gas mixture is effected in a column of 6 m length and 12 mm diameter. In this way a pressure rise of 0.1 atm is obtained in a 1-litre receiver. On account of the vapour tension of the KOH solution and with a view to proper functioning of the absorber, the initial pressure cannot be chosen lower than 0.1 atm; consequently, the final pressure is *ca.* 0.2 atm.abs. At this pressure the percentage of C_5 and C_6 hydrocarbons in the gas mixtures, which are usually low, are still easily determined and no trouble is caused by condensation or deviation from the ideal gas laws.

The pressure at the end of the column is adjusted with a release valve and is independent of the changes in pressure in the receiver. The velocity of the stripper gas is controlled by means of the gas pressure at the inlet of the column.

The possibilities offered by the apparatus have not yet all been ascertained, but it seems likely that the components and fractions separated can be determined with an accuracy of at least ±0.3% on the total sample.

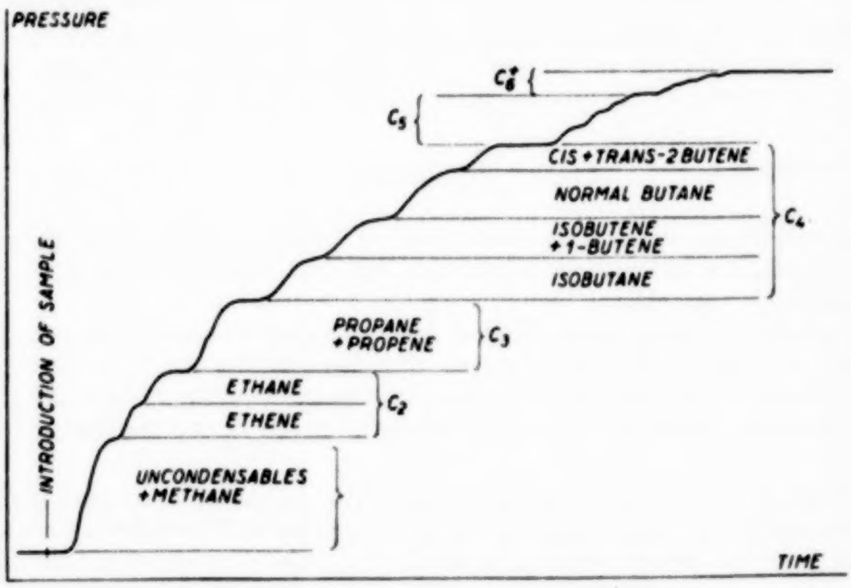

Fig. 7. Analysis of a full-range cracked gas.

Fig. 7 gives an example of the analysis of a gas obtained by catalytic cracking of a petroleum fraction. In order to effect a satisfactory separation of the light components and yet complete the analysis in an hour's time use was made of a long column (6 m), the temperature of which, during the analysis, was gradually increased from +20° C to +80° C. In this case the stationary liquid phase was liquid paraffin.

As is shown by this example the method is particularly suitable for the analysis of gas mixtures consisting of a large number of components comprising a wide boiling range. For the analysis of simple mixtures or the accurate determination of low concentrations ($<$ 1%) the thermal conductivity method is, however, preferable.

On the strength of the experience gained with vapour phase chromatography in the past few years, it appears justified to expect that this method will come to occupy an important place among the many other physical methods for the analysis of hydrocarbon gases and other volatile products, such as low-temperature distillation, infrared, ultraviolet and mass spectrometry.

On account of its relatively low cost, its simplicity of operation and the rapid interpretation of the results, chromatography is an ideal method for production control.

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SUMMARY

Of the various types of gas chromatography developed in the past few years gas-liquid partition chromatography has been found to be the best method for the analysis of hydrocarbon gases.

By a suitable choice of the liquid phase and the other conditions,it is possible to separate each individual hydrocarbon in the C_1-C_5 range from the other components. The influence of size of column nature of carrier material, concentration of liquid phase on carrier, and gas velocity, has been discussed.

For the quantitative determination of the components two methods were used, *viz.*:

(a) Continuous measurement of the thermal conductivity of the gas mixture leaving the column. This method is preferred for the analysis of gas mixtures consisting of a limited number of components and for the determination of a single component in a complex mixture.

(b) Measurement of the pressure increments obtained by collecting the components in an evacuated vessel after the CO_2 stripper gas has been removed by absorption in a caustic solution. This method is particularly suitable for the analysis of gas mixtures consisting of many components with widely different boiling points.

RÉSUMÉ

Parmi les différents types de chromatographie en phase gazeuse, mis au point ces dernières années, la chromatographie de partition gaz-liquide s'est trouvée être le meilleur moyen pour l'analyse d'hydrocarbures gazeux.

Par un choix judicieux de la phase liquide et des autres conditions, il est possible d'isoler chaque hydrocarbure dans la série C_1-C_5. L'influence des dimensions de la colonne, de la nature du support, du pourcentage de la phase liquide sur le support, et de la vitesse des gaz a été examinée.

Pour la détermination quantitative des composants, deux méthodes ont été employées, à savoir:

(a) La mesure en continu de la conductibilité thermique du mélange gazeux sortant de la colonne. On préfère cette méthode pour l'analyse de mélanges gazeux constitués d'un nombre limité de composants et pour la détermination d'un seul composant dans un mélange complexe.

(b) La mesure de l'accroissement de pression, obtenu en recueillant les composants dans un récipient évacué, après l'élimination du CO_2 par absorption dans une solution de potasse caustique. Cette méthode convient particulièrement bien à l'analyse de mélanges constitués de nombreux composants présentant une grande différence de points d'ébullition.

ZUSAMMENFASSUNG

Es hat sich herausgestellt, dass von den verschiedenen in letzter Zeit entwickelten Arten der Gaschromatographie die Gas-Flüssigkeits-Verteilungschromatographie das beste Hilfsmittel für die Analyse von Kohlenwasserstoffgasen ist.

Bei geeigneter Wahl der flüssigen Phase und der übrigen Bedingungen ist es möglich, jeden einzelnen Kohlenwasserstoff der C_1-C_5 -Reihe von den anderen zu trennen. Der Einfluss der Dimensionen der Kolonne, der Art des Trägermaterials, der Konzentration der flüssigen Phase auf dem Träger und der Gasgeschwindigkeit wurde bestimmt.

Zur quantitativen Bestimmung der Komponenten kamen zwei Methoden zur Anwendung, und zwar:

(a) Ununterbrochene Messung der Wärmeleitfähigkeit des aus der Kolonne tretenden Gasgemisches. Diese Methode hat den Vorzug für die Analyse von Gasgemischen mit einer beschränkten Anzahl Komponenten und für die Bestimmung einer einzigen Komponente in einem Mehrkomponentengemisch.

(b) Messung der Drucksteigerungen, die durch Sammlung der Komponenten in einem evakuierten Gefäss, nachdem das CO_2-Gas durch Absorption in Lauge entfernt worden ist, bewirkt werden. Diese Methode eignet sich besonders zur Analyse von Gasgemischen, die aus vielen Komponenten eines sehr weiten Siedebereiches bestehen.

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THE USE OF OXALYLDIHYDRAZIDE IN A NEW REACTION FOR THE SPECTROPHOTOMETRIC MICRODETERMINATION OF COPPER

by

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Some years ago NILSSON[1] noticed that an intensive blue-violet to violet color was obtained if a very weak solution of a copper salt was mixed with ammonium hydroxide, oxalyldihydrazide, and a large excess of formaldehyde or acetaldehyde. NILSSON suggested that the color obtained in this new reaction might be more intensive and less sensitive to changes in the pH value of the solution than that obtained in a reaction with bis-cyclohexanone-oxalyldihydrazone previously described[2,3]. Some qualitative data about the new reaction will be published by NILSSON in the near future.

With these reasons in mind an investigation was started to find a highly sensitive, selective and specific spectrophotometric method for the determination of microamounts of copper (5 to 50 μg).

I. Oxalyldihydrazide and formaldehyde

Solutions

1. *Standard copper solution.* A solution containing 6.0 mg of Cu^{+2} per litre.
2. *Oxalyldihydrazide.* A saturated solution. Excess reagent is dissolved in hot water. After cooling the clear solution is decanted from the crystals.
3. *Ammonium hydroxide.* A concentrated solution.
4. *Formaldehyde.* A 40% solution.

The preparation of the oxalyldihydrazide is very simple[4]. Equimolecular amounts of a diester of oxalic acid and of hydrazine hydrate, each dissolved in five volumes of alcohol, are mixed. In less than an hour a nearly quantitative yield is obtained. The product is washed with a little alcohol and recrystallized from boiling water.

NILSSON suggested[1] that the order of mixing the solutions might have a pronounced effect upon the color intensity. The optimal proportions of the reagent solutions were ascertained in a few trial runs, and then a series of experiments was carried out where the order of addition of the four reagents was varied in the twenty four possible ways: 10 ml portions of each solution were added successively to a 50 ml volumetric flask which was then filled to the mark with distilled water. The absorbancy was measured at 565 mμ in a Beckman spectrophotometer model B. A statistical analysis of the values obtained showed that the formaldehyde should be added later than all the other reagents.

The order of addition of the remaining solutions was unimportant, and it was choosen to add them in the order: copper solution, ammonium hydroxide, and oxalyldihydrazide.

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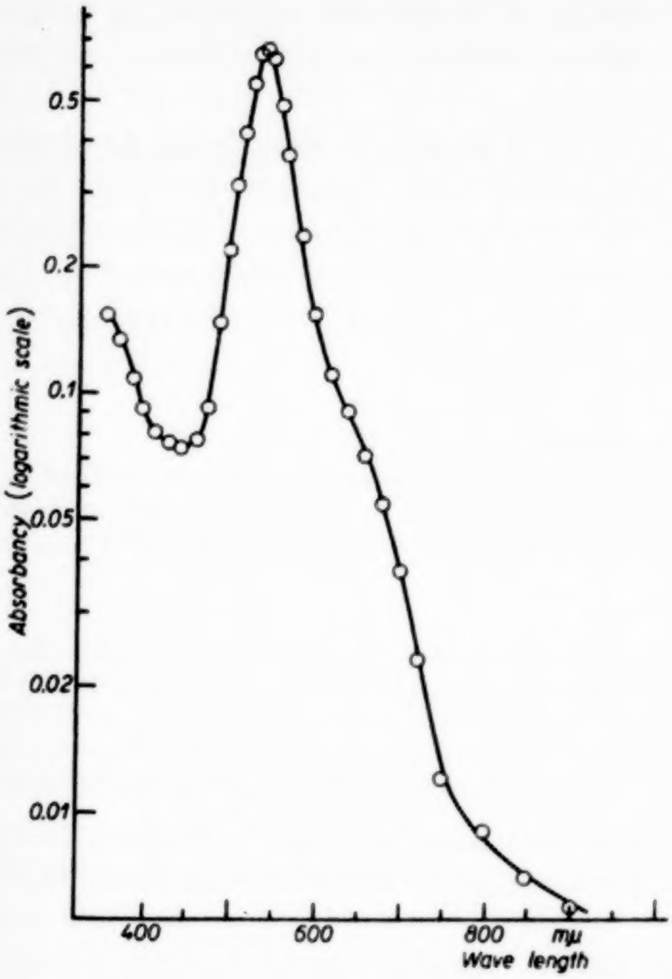

Fig. 1. Absorbancy curve for the violet color obtained in mixing a copper solution with ammonium hydroxide, oxalyldihydrazide and acetaldehyde.

It was found that the most intensive color is obtained when the pH value of the solution is in the range 5 to 10. Above pH 10 the color intensity diminishes rapidly with increased alkalinity. In the range 3 to 5 the color intensity seems to depend on the kind of acid used for buffering the solution. Phosphoric acid seems to decrease the color intensity much more than do acetic and hydrochloric acid.

II. Oxalyldihydrazide and acetaldehyde

Solutions

1 — 3. Same as before.
5. *Acetaldehyde.* A 40% solution.

According to NILSSON's findings[1], the color obtained with acetaldehyde instead of formaldehyde has a violet tinge. The absorbancy was measured as a function of the wavelength on a solution prepared by mixing:

10 ml of a copper solution (60 μg Cu^{+2})
5 ml of conc. ammonium hydroxide
4 ml of a saturated oxalyldihydrazide solution
10 ml of a 40% acetaldehyde solution
and diluting to 50 ml in a volumetric flask.

The curve found is shown in Fig. 1. The maximum, which is situated at about 542 mμ, is much more pronounced and much higher than with formaldehyde and it is also much more pronounced than in the reaction with bis-cyclohexanone-oxalyldihydrazone and gives a value for the molar absorbancy index of about $\varepsilon = 29{,}500$ or $\log \varepsilon = 4.47$. This is most certainly the highest value hitherto found for any copper reagent.

In the same way a series of experiments was made where the concentration of copper was varied. The absorbancy is plotted versus copper concentration in Fig. 2. It is obvious that Beer's law is followed very closely.

The color obtained is very stable. It increases during the first few minutes but after about 30 minutes it remains stable for at least several hours.

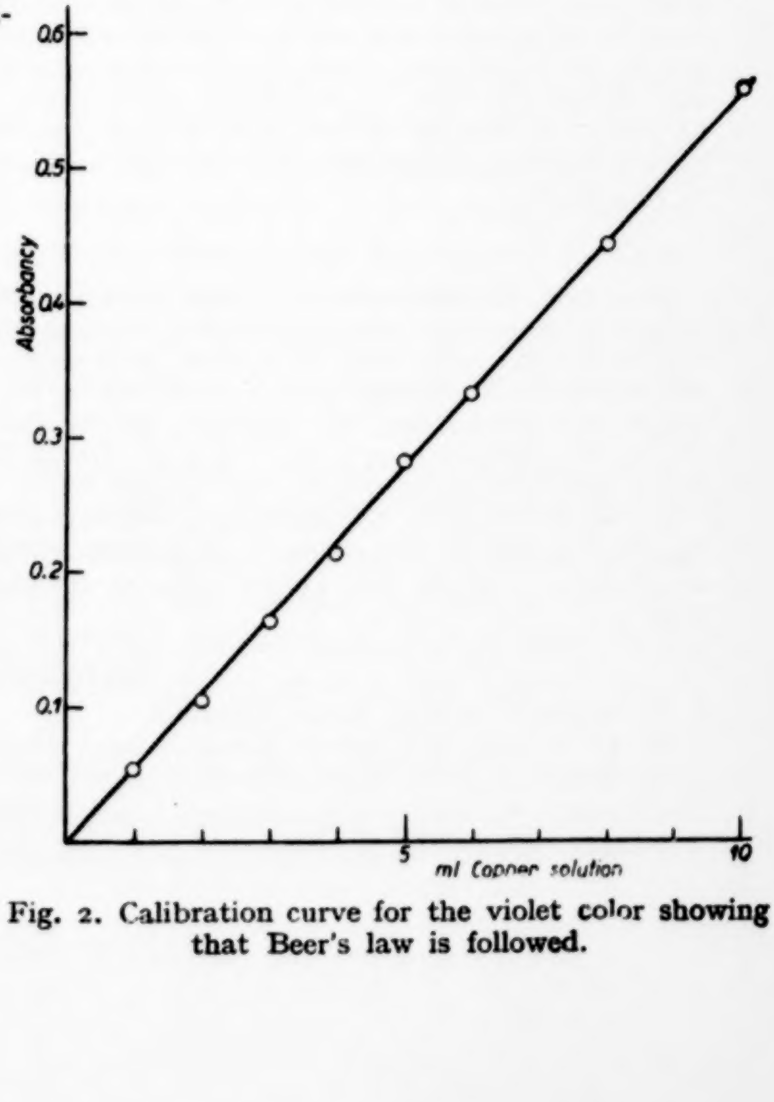

Fig. 2. Calibration curve for the violet color showing that Beer's law is followed.

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Some experiments showed that the presence of reasonable amounts of hydrochloric, nitric, and perchloric acid or of sodium sulfate had no influence on the absorbancy.

As reagent grade acetaldehyde could only be supplied in anhydrous form and was therefore fairly expensive, a regular grade and also a purified product[5] were tested. Fortunately no difference in absorbancy or other properties of the colored solutions could be detected. The small amounts of impurities encountered in the regular grade aldehyde therefore do not seem to have any influence on the reaction or the stability of the color.

ACKNOWLEDGEMENT

The author wants to thank civ.-ing. G. NILSSON, Chemical Laboratory, Department of Building Technique, Royal Institute of Technology, Stockholm, for valuable discussions and for many suggestions during this investigation and also for a supply of highly purified acetaldehyde.

SUMMARY

A new reaction for the spectrophotometric microdetermination of copper is described. To a strongly ammoniacal solution containing traces of copper is added a saturated solution of oxalyldihydrazide and formaldehyde or preferably acetaldehyde. A blue-violet to violet color of unusually high intensity is obtained. The absorbancy maximum is situated at about 542 mμ and the molar absorbancy index has a value of about 29,500 (log ε = 4.47). This value is most certainly the highest hitherto known for any copper reagent.

The order of addition of the reagents is of great importance. The aldehyde should definitely be added last. The purity of the aldehyde does not seem to be of any great importance for the intensity or stability of the color.

RÉSUMÉ

Une nouvelle réaction pour le microdosage spectrophotométrique du cuivre est décrite. A une solution fortement ammoniacale renfermant des traces de cuivre, on ajoute une solution saturée d'oxalyldihydrazide et de formaldéhyde, ou mieux d'acétaldéhyde. Une coloration bleu violet à violette d'une extraordinaire intensité est obtenue. L'absorption maximum se trouve à environ 542 mμ et le coefficient d'extinction moléculaire est d'environ 29,500 (log ε = 4.47). Cette valeur est très certainement la plus élevée parmi celles des réactifs du cuivre connus actuellement. L'ordre d'addition des réactifs est très important. L'aldéhyde doit absolument être introduit le dernier. La pureté de l'aldéhyde ne semble pas jouer un grand rôle sur l'intensité ou la stabilité de la coloration.

ZUSAMMENFASSUNG

Eine neue Reaktion für die spektrophotometrische Mikrobestimmung von Kupfer wird beschrieben. Eine stark ammoniakalische, kupferhaltige Lösung wird mit einer gesättigten Lösung von Oxalyldihydrazid und mit Formaldehyd oder — noch besser — Acetaldehyd versetzt. Dabei entsteht eine blauviolette bzw. violette Farbe von ausserordentlich hoher Intensität. Das Absorptionsmaximum liegt bei ungefähr 542 mμ und der molare Absorptionskoeffizient hat einen Wert von ungefähr 29,500 (log ε = 4.47). Dieser Wert ist wahrscheinlich der grösste, der bisher für Kupferverbindungen gefunden worden ist.

Die Reihenfolge, in der die Reagenzien zugesetzt werden, ist von entscheidender Bedeutung für die Farbstärke. Die Aldehydlösung muss unbedingt zuletzt zugesetzt werden. Die Reinheit des Aldehyds scheint von untergeordneter Bedeutung für Stärke und Stabilität der Farbe zu sein.

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COLORIMETRIC DETERMINATION OF TRACES OF TIN WITH DITHIOL

by

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The work described here was done to provide a color method for determining traces of tin in natural materials. Available photometric procedures are intended for amounts of tin greater than about 40 γ, and are not applicable without modification to such samples.

At the present time an entirely satisfactory colorimetric reagent for tin is lacking. Dithiol appears to be the best of a number of reagents that have been used for the determination of relatively small amounts of tin. Both on the basis of sensitivity and selectivity it is superior to 8-hydroxyquinoline, cacotheline, diethyldithiocarbamate and hematoxylin. Although tin is usually separated from other elements by distillation procedures before determination, traces of heavy metals may be introduced in the subsequent treatment of the distillate and can cause trouble if the colorimetric reagent is not selective and minimal amounts of tin are to be determined. Dithiol reacts with many metals in acidic solution but the reaction products do not have the characteristic bright red color of tin(II) dithiolate.

When tin dithiolate is extracted by suitable organic solvents the color of the extract is pale yellow and not red, and immiscible solvent extraction does not appear to have any advantage. A colloidal dispersion of tin dithiolate must therefore be used for photometry or colorimetry[1,2,3]. Such methods have certain disadvantages. However, the present work has shown that a fairly satisfactory determination of 3 to 50 γ or more of tin can be made photometrically in this way (error usually less than 10% with more than 20 γ). Below 3 γ, a visual comparison method enables tin to be determined to $\pm$ 0.5 γ. The concentration sensitivity of the present procedure with a 1 g sample is 0.5 p.p.m., which is at least as good as the best arc spectrographic methods in use today.

The procedure described below was worked out with silicate rocks and meteorites particularly in mind, but it should be quite generally applicable. The separation of tin is made in the standard way, by distillation from hydrobromic acid solution.

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Apparatus

The distilling flask is a modification of SCHERRER's[4]. By means of a 34/45 standard taper joint the upper portion carrying the separatory funnel, thermometer well, and outlet tube is fitted to a 200 ml round-bottomed flask. The condenser (30 cm in length) is connected to the side arm by a 12/30 standard taper joint.

Solutions

Water, redistilled in Pyrex.

Nitric acid, concentrated, distilled in Pyrex.

Hydrochloric acid, 6*N*. Dilute the concentrated acid with an equal volume of water and distil.

Hydrobromic acid, 48%. Distil in Pyrex, rejecting the first and last 1/5.

Sulfuric acid. Volatilize possible traces of tin by adding dropwise a mixture of 15 ml of 6*N* hydrochloric acid with 2 ml of hydrobromic acid to 100 ml of 1 : 1 sulfuric acid and 10 ml of 6*N* hydrochloric acid at 150-160° C. Then add 10 ml of 6*N* hydrochloric acid drop by drop at the same temperature. Finally boil the sulfuric acid for another 10 minutes, cool, and dilute to 100 ml with water. Great care must be taken to remove all hydrobromic acid.

Dithiol, 0.1 g in 50 ml of 1% sodium hydroxide. Add 0.3-0.5 ml of thioglycolic acid as stabilizer. The solution may be used for a week if kept in a refrigerator.

Thioglycolic acid, at least 80% strength. Avoid the use of old products.

Santomerse S (Monsanto Chem. Co.). (1) Dilute 10 ml of the 30% solution to 40 ml with water (1 : 3). (2) Dilute 2 ml of the 30% solution to 40 ml with water (1 : 19).

Selenious acid, 1 mg Se per ml. Treat 100 mg of selenium with 1 to 2 ml of concentrated nitric acid and evaporate to dryness. Add 1 ml of concentrated hydrochloric acid and again evaporate to dryness. Dissolve the residue in 10 ml of concentrated hydrochloric acid and dilute to 100 ml with water.

Sulfurous acid. Prepare fresh daily by saturating water with sulfur dioxide.

Standard tin solutions. Dissolve 0.100 g of tin in 10 ml of concentrated hydrochloric acid and dilute to 100 ml with water after adding 0.5 ml of thioglycolic acid (1.00 mg Sn per ml). This solution may be kept for 2 weeks. (1) 100 γ Sn per ml solution. Dilute 10 ml of the stock solution to 100 ml with 1 : 19 hydrochloric acid. This solution can be kept for 2 days. (2) 10 γ Sn per ml solution (1 : 19 hydrochloric acid). Prepare fresh daily.

PROCEDURE

General directions for distillation and determination of tin

Transfer the sample solution to the distilling flask with 25 ml of 1 : 1 sulfuric acid, 5 g of KH_2PO_4 (or 3 ml of 85% phosphoric acid)*, 20 ml of 6*N* hydrochloric acid and 1 g of hydrazine sulfate.

Dip the end of the condenser into 30 ml of water in a 150 or 250 ml beaker. Pass a slow stream of carbon dioxide through the solution and boil gently. When the temperature has reached 160° C, introduce 6*N* hydrochloric acid dropwise at a rate of 1 drop every 4 seconds while maintaining the temperature at 155 to 165° C. When about 20 ml of hydrochloric acid has been added, remove the burner and beaker after washing the stem of the condenser with water. Discard the distillate and washings (contain arsenic).

Place a 100 ml beaker containing 15 ml of cold water under the condenser. Add a mixture of 15 ml of 6*N* hydrochloric acid and 7 ml of hydrobromic acid drop by drop while maintaining the temperature at 145 to 160° C and passing in carbon dioxide. This requires 15 to 20 minutes. Remove the burner, lower the beaker, and wash down the stem of the condenser.

To the distillate add 0.50 ml of 1 : 2 sulfuric acid and 5 ml of concentrated nitric acid and heat covered on a steam bath or a low temperature hot plate. When vigorous reaction has ceased, remove the cover glass, evaporate to a small volume, and finally fume for 3 to 5 minutes.

If the amount of tin is expected to exceed 3 γ, apply the photometric method: Add 4 ml of water and transfer the solution to a 10-ml volumetric flask and make up to about 7 ml with water. Add 1 drop of thioglycolic acid and mix. Add 0.05 ml of 1 : 19 Santomerse S, swirl gently, add 0.50 ml of dithiol solution and mix. Heat at 50 ± 5° C in a water bath for 5 ± 1 minutes. Then add 0.5 ml of 1 : 3 Santomerse S and mix. Cool, dilute to the mark with water, and mix. Measure the absorbance at 530 mμ without undue delay. Establish the standard curve by taking 0, 5, 10, 30, and 60 γ of tin, adding 0.50 ml of 1 : 2 sulfuric acid, and proceeding as described above. To obtain the reagent blank, run 5.0 γ of tin through the whole procedure and deduct 5.0 γ from the amount of tin found.

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* Potassium phosphate is preferred because of its lower tin content, but when the lowest possible blank is not required, phosphoric acid can be used, and has the advantage that it has no tendency to cause bumping.

When tin is less than about 3 γ use the visual comparison method: Add 2 ml of water to the sulfuric acid residue, transfer the solution to a 15-ml porcelain crucible, and wash the beaker with 1-ml portions of water. Evaporate to a drop by fuming. If the solution shows a brown color due to the presence of organic matter, add 0.1 g of ammonium persulfate and fume for a few minutes. Cool, add 0.25 ml of water, 1 drop of 1 : 5 thioglycolic acid (prepared immediately before use) and 1 drop of dithiol solution and mix. Heat on the steam bath for 3 minutes. Cool and compare the pink color with standards obtained by taking, *e.g.*, 0, 0.5, 1.0, 2.0, and 3.0 γ Sn, adding 0.50 ml of 1 : 2 sulfuric acid, fuming to a drop, and treating in the same way as the unknown.

Silicate rocks. The following directions are for silicate samples completely decomposable by hydrofluoric acid. Add 5 ml of 1 : 1 sulfuric acid, 0.5 to 1 ml of concentrated nitric acid, and 10 ml of hydrofluoric acid to 1.0 g of 100-mesh rock powder in a platinum dish and evaporate to strong fumes of sulfuric acid. Cool, add 1 ml of 1 : 1 sulfuric acid and 1-2 ml of water, and again evaporate to strong fumes. Transfer the residue with 25 ml of 1 : 1 sulfuric acid, 5 g of KH_2PO_4, 1 g of hydrazine sulfate and 10 ml of 6*N* hydrochloric acid to the distilling flask, and continue as in the general procedure above (usually by the visual method).

If cassiterite or other minerals not decomposed by hydrofluoric acid may be present, add to the residue from the hydrofluoric acid treatment 10 ml of 6*N* hydrochloric acid and 20 ml of water. Heat to near the boiling point and keep at this temperature until almost complete solution has been obtained. Filter through a medium-textured paper and wash with 2*N* hydrochloric acid and finally with water. Catch the filtrate and washings in the distilling flask.

Ignite the paper in a nickel crucible at a low temperature. Fuse the residue gently with 0.5 g of sodium hydroxide, and keep at dull redness for 30 minutes. Cool, and dissolve the melt in 8 ml of water. Transfer the solution to a beaker and carefully add 10 ml of 6*N* hydrochloric acid. Heat on a low-temperature hot plate for a few minutes and filter off the insoluble matter on a small medium-textured paper and wash the residue with 2*N* hydrochloric acid. Catch the filtrate and washings in the same distilling flask or carry out the distillation separately. If the tin content has been found to be relatively high (*e.g.* > 20 p.p.m.), fuse the residue again with sodium hydroxide and treat as described above. If much cassiterite is present, the preceding treatment may not recover all the tin. See DISCUSSION.

Iron (steel, iron meteorites). Dissolve 0.5 g of sample (1-100 p.p.m. Sn) in 7 ml of 1 : 1 sulfuric acid and 10 ml of 1 : 1 nitric acid. Evaporate and fume for a few minutes. Transfer the residue with 25 ml of 1 : 1 sulfuric acid, 5 g KH_2PO_4 (or 3 ml of 85% phosphoric acid), and 20 ml of 6*N* hydrochloric acid to the distilling flask containing 1 g of hydrazine sulfate. Carry out the distillation as described above. If the tin content of sample is likely to be less than 6 p.p.m. Sn use the visual method described above.

*Sulfides.** Treat 1.0 g of sample (0.5-50 p.p.m. Sn) with 10 ml of fuming nitric acid in a 100-ml beaker. Heat gently at first. When vigorous reaction has ceased, evaporate to a volume of 1 to 2 ml. Cool, add 7 ml of 1 : 1 sulfuric acid, and evaporate to strong fumes. Transfer the residue with 25 ml of 1 : 1 sulfuric acid, 5 g of KH_2PO_4 or 3 ml of 85% phosphoric acid, and 20 ml of 6*N* hydrochloric acid to the distilling flask containing 1 g of hydrazine sulfate. Carry out the distillation and determination of tin as described above (visual method for less than 3 p.p.m. Sn).

If selenium is likely to be present (*e.g.*, pyrite) treat the distillate as follows. After evaporation and fuming for 3 to 5 minutes, cool, add 4 ml of 6*N* hydrochloric acid and 0.1 ml of selenious acid (0.1 mg Se) and heat on a low temperature hot plate for about 5 minutes. Cool to room temperature, add 2 ml of saturated sulfurous acid and 0.2 g of hydroxylamine hydrochloride. Heat at 90° C for 1/2 to 1 hour. Collect the precipitate in a small porcelain filter crucible and wash with 1 : 99 hydrochloric acid, catching the filtrate and washings in a small beaker. Evaporate to fumes of sulfuric acid. Cool, add 2 ml of water, filter through a filter crucible, and wash with water. Catch the filtrate and washings in a 10-ml volumetric flask or a crucible depending on the expected amount of tin. Then continue as in the general procedure above.

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* This procedure is not intended for galena, the lead sulfate from which might retain tin. This point has not been tested.

DISCUSSION

Photometric and colorimetric determination of tin.

All the photometric procedures utilize a protective colloid to disperse stannous dithiolate. We have followed FARNSWORTH AND PEKOLA[3] in using Santomerse S for this purpose, but have introduced a number of changes.

With hydrochloric acid for acidification, a concentration of 0.4 to 0.6N is the most suitable, with sulfuric acid, a concentration of 0.4 to 0.8N. If the acidity is too high, Santomerse S is precipitated. If too little Santomerse S is present when dithiol is added, it is difficult to obtain a clear solution, even if more dispersing agent is added later. On the other hand, if its concentration is initially too high, color development is hindered. Thus 10 γ of tin will not give a color when 0.1 ml of 1 : 3 (v/v) Santomerse S is added. We have found that the most satisfactory procedure is to develop the color in the presence of a small amount of the dispersing agent and then to add more to stabilize the suspension.

Heating is required for rapid, full color development, when less than 20-30 γ tin is present in 10 ml. Heating at 100° with these amounts of tin causes decoloration after about a minute. This fading does not take place if the temperature is reduced to 50°. For more than about 30 γ of tin, color development at room temperature is satisfactory.

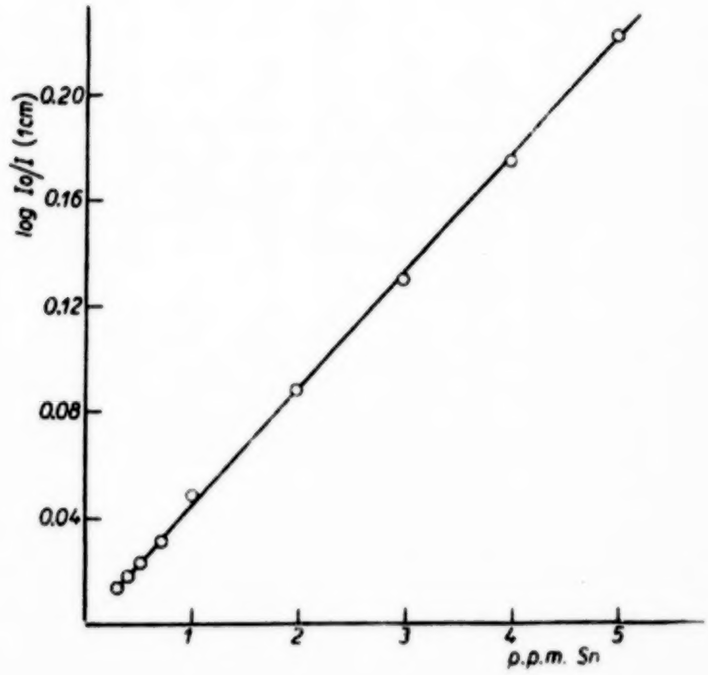

Fig. 1. Absorbance-concentration curve for determination of tin with dithiol (Leitz-Rouy photometer, 535 mμ filter). No color is produced below ~0.3 p.p.m. Sn in solution.

Under the conditions recommended, absorbance is proportional to tin concentration in the range 0.25 to 6 p.p.m. or higher (Fig. 1). Below 0.25 p.p.m. Sn no color is produced. A number of factors may contribute to this: solubility of tin dithiolate, formation of supersaturated solutions, and inhibition of nucleation and particle growth by the dispersing agent. Therefore the photometric method fails when the tin concentration is less than 2.5 γ in 10 ml of final solution. To determine smaller amounts of tin it is necessary to reduce the volume of solution. This is conveniently done by using porcelain crucibles, developing the color in a volume of a few tenths of a milliliter without using a dispersing agent, and visually comparing the color with standards obtained similarly. As little as 0.5 γ of tin can be detected in this way. This procedure is simpler than collecting the tin precipitate on a disk of filter paper and comparing with similar standards (as done by SCHWAIBOLD *et al.*[10], and JANTSCH *et al.*[11]) and sufficiently accurate for small amounts of tin.

TABLE I

INTERFERENCE OF SOME IONS (DIRECT TEST)

Addition, γ	*Sn taken, γ*	*Sn found, γ*	*Remarks*
50 As	0	0.5, $<$0.5	
50 As	20.0	20.0, 20.0	100 γ As interferes (ppt.)
10 Sb	0	$<$0.5, $<$0.5	
10 Sb	20.0	20.5, 21.0	50 γ Sb interferes
5 Bi	0	2	5 γ Bi interferes
5 Bi	20.0	22.5	
10 Bi	0	3	
10 Bi	20.0	24	
90 Ge	0	$<$0.5, 0.0	
90 Ge	20.0	21.0, 19.0	
5 Mo	0	5	Mo interferes seriously
5 Mo	20	24.5	
10 Mo	0	7	
10 Mo	20.0	28	
50 Hg	0	0	1000 γ Hg gives ppt.
50 Hg	20.0	20.5	
10 Se	0	$<$0.5	50 γ Se gives white ppt. or turbidity
10 Se	20.0	20.5	
10 Te	0	$<$0.5	50 γ Te interferes (brown color)
10 Te	20	19.5	

TABLE II

SUMMARY OF CONDITIONS OF TIN BROMIDE DISTILLATION

Volume ratio HBr/HCl*	*Temperature °C*	*Amount of tin*	*Author*
HBr only	220	0.25–2.5 mg	LAW[5]
6	180–185	10–200 mg	MOGERMAN[6]
2	137–147	0.04–0.8 mg	FARNSWORTH AND PEKOLA[3]
1/3	140	∿10 mg	SCHERRER[7]
1/3	130–140	Milligram quantities	KLINGER *et al.*[8]
1/3	135–145	—	BILTZ AND BILTZ[9]
1/3	130–140	Microgram quantities	SCHWAIBOLD *et al.*[10]
1/3	—	Microgram quantities	JANTSCH *et al.*[11]

* Of the concentrated acids. Sulfuric acid present in all to raise distillation temperature.

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The effect of a few elements, particularly some that can be volatilized in distillation procedures, on the direct determination of tin was tested (Table I). Less than 50 γ of arsenic, germanium, and mercury or $\sim$ 10 γ of antimony, selenium and tellurium do not interfere, so that the separation of these elements need not be sharp. Molybdenum (green color) interferes seriously in very small amounts, and bismuth (reddish-brown color) almost as much.

TABLE III

BROMIDE DISTILLATION OF TIN

*Acid mixture**	*Temperature* °*C*	*Time min*	*Sn taken* γ	*Sn found* γ
14 ml HBr + 7 ml HCl	131–38	16	30	18
14 ml HBr + 7 ml HCl	131–38	25	30	18**
14 ml HBr + 7 ml HCl	147–60	25	30	28
10 ml HBr + 5 ml HCl	147–60	18	23	20
7 ml HBr + 7 ml HCl	150–60	18	20	16
7 ml HBr + 3.5 ml HCl	147–60	15	30	23
10 ml HBr + 10 ml HCl	150–60	25	30	30
7 ml HBr + 14 ml HCl	155–60	20	30	32
5 ml HBr + 15 ml HCl	140–50	25	23	20
5 ml HBr + 15 ml HCl	150–55	25	30	30

* HBr sp. gr. *ca.* 1.38, HCl 1.19; 30 mg of Fe(III) to oxidize Sn(II).
** Another 21 ml portion of HBr + HCl distilled at 147–57° yielded 16 γ Sn.

Separation of tin

The familiar hydrobromic-hydrochloric acid distillation is used. The conditions of distillation employed by earlier workers are summarized in Table II. From previous results and those of a few experiments carried out here (Table III) it may be concluded that HBr/HCl ratios (by volume of concentrated acids, sp.gr. HCl 1.19, sp.gr. HBr 1.38) from 2 to about 1/3 give equally good results. We have adopted a 1 : 1 ratio, with distillation at 150-160°.

By first distilling from hydrochloric acid solution at 160°, arsenic, antimony and germanium can be removed, so that they do not accompany tin in the hydrobromic-hydrochloric acid distillation. The only element giving trouble is selenium, which partly accompanies tin in the hydrobromic acid distillation and gives a white precipitate or turbidity in the subsequent dithiol determination if its amount is greater than about 10 γ. The remedy for this is precipitation of selenium with sulfur dioxide in the distillate. To assure the formation of a coagulable precipitate, 0.1 mg of Se (IV) is first added.

Before tin can be determined in the distillate, the solution must be evaporated to remove the excess acid. FARNSWORTH AND PEKOLA used hydrogen peroxide to decompose hydrobromic acid. In our hands, this procedure resulted in the loss of tin. Nitric acid was found to be entirely satisfactory for the purpose.

The results in Table IV demonstrate that tin can be satisfactorily separated and determined by the recommended procedure in the presence of arsenic, bismuth,

TABLE IV

PHOTOMETRIC DETERMINATION OF TIN AFTER DISTILLATION

Addition	*Sn taken* γ	*Sn found** γ
30 mg Fe	0.0	0
30 mg Fe	3.0	3.5, 3.5
30 mg Fe	5.0	5.0, 5.0
60 mg Fe	10.0	9.5, 10.0
30 mg Fe	30.0	28.5
100 γ As, 50 γ Bi, 30 mg Fe, 100 γ Mo, 50 γ Sb, 1000 γ W	0.0	0
100 γ As, 50 γ Bi, 30 mg Fe, 100 γ Mo, 50 γ Sb, 1000 γ W	10.0	10.0, 10.0
100 γ As, 50 γ Bi, 30 mg Fe, 100 γ Mo, 50 γ Sb	0.0	0
100 γ As, 50 γ Bi, 30 mg Fe, 100 γ Mo, 50 γ Sb	20.0	19.5
15 mg Fe, 50 γ each Hg, Se, Te	0.0	0
15 mg Fe, 50 γ each Hg, Se, Te	20.0	19.5
12 γ Ru(IV), 10 γ Os(VIII), 10 γ Re(VII)	0.0	0
12 γ Ru(IV), 10 γ Os(VIII), 10 γ Re(VII)	20.0	17.5
0.1 mg Se**	0	0.5, 0.5
0.1 mg Se**	20.0	20.5

* Correction applied for blank (4.0 γ) which was determined by adding 5 γ Sn and deducting (see text). Includes other metals reacting with dithiol, introduced after distillation (chiefly in nitric acid). Since a blank without added tin showed no pink color, the actual tin content is less than $\sim 3\ \gamma$.

** Selenium (as selenious acid) added to distillate and precipitation made with sulfur dioxide and hydroxylamine hydrochloride as described under sulfides in PROCEDURE.

TABLE V

DETERMINATION OF TIN IN SILICATE ROCK, IRON METAL, AND PYRITE

Sample	*Method*	*Sn present* *p.p.m.*	*Sn found* *p.p.m.*
Quartz monzonite*	Visual	2.3	2.0, 2.5
	Visual	3.3	3.5
	Photometric	6.3	5.0, 5.0
	Photometric	11	12
	Photometric	21	18.5
	Photometric	31	29
Iron ("Puron")**	Visual	2	2
	Visual	6	6
	Photometric	20	24
	Photometric	40	38
Pyrite***	Photometric	20	20.5

* 1 g sample; original Sn content 1.3 p.p.m. (average of 1.0 and 1.5 p.p.m.); blank in visual method 2 p.p.m. Sn, in photometric method 6.5 p.p.m.

** 0.5 g sample; contained no detectable tin; 0.1% Co, 0.02% Cr, 0.01% Cu added; blank in visual method 1 p.p.m. Sn, in photometric method 9 p.p.m.

*** Leadville, Colo.; 1 g sample; original tin content 0 p.p.m.; selenium separated as described in PROCEDURE.

molybdenum, tungsten, selenium and tellurium in such amounts as are likely to be encountered in silicate rocks, sulfides and meteorites. Table V shows that good recoveries of tin can be obtained from such materials.

When the reagent blank is run in the photometric method, a small amount of tin (3-5 γ) must be added to make certain that the tin concentration in the final solution will be above 3 p.p.m. Below this value, as already mentioned, no coloration is obtained, and it might therefore happen if no tin were added in the blank run that no tin would be shown, although some is present in the reagents and is adding its effect to the tin in the sample. The photometric blank is the sum of the absorbance due to tin and to possible traces of other metals giving colored or slightly soluble products with dithiol. In the present work a blank of 4 γ apparent tin was found with analytical-reagent nitric acid and ordinary distilled water, and of 3 γ apparent tin with nitric acid and water redistilled in Pyrex. By using purified hydrobromic acid, hydrochloric acid, sulfuric acid, and nitric acid, and substituting KH_2PO_4 (5 g) for 85% phosphoric acid, the photometric blank was reduced to 1 γ.

When the blank is run in the visual comparison method, tin need not be added. The blank in the visual method should not exceed 0.5 γ Sn when reagents purified as described are used.

It should be pointed out that a greenish off-color will be obtained in the visual method if the concentration of sulfuric acid is too high. Therefore it is important to fume down to a drop before color development. The final dilution to 0.4-0.5 ml takes care of any small variation in the amount of residual sulfuric acid. It is preferable to treat the standards at the same time as the sample solution so that one can more easily obtain the same final volume of sulfuric acid. The hue of sample and standards should be practically the same.

When the sample contains cassiterite, complete decomposition is not obtained even if the residue from the hydrofluoric-sulfuric acid decomposition is fused several times with sodium hydroxide, as shown by the following results. Finely ground cassiterite-bearing pegmatite (0.5 g) was treated with hydrofluoric and sulfuric acids as described above. The residue was treated with 2-3*M* hydrochloric acid and the insoluble matter was filtered off. It was fused at dull redness with sodium hydroxide in a nickel crucible:

	per cent Sn found		
	(1)	(2)	(3)
After HF + H_2SO_4 decomposition	0.0048	0.0055	0.0056
After 1st NaOH fusion	—	0.15	0.11
After 2nd NaOH fusion	—	0.036	0.039
After 3rd NaOH fusion	—	0.011	0.021
After 4th NaOH fusion	—	—	0.012
Total		0.203	0.188

When 0.5 g of the same sample was first fused with sodium hydroxide or other

flux, followed by hydrofluoric-sulfuric acid treatment, the following results were obtained:

	per cent Sn found		
Flux	NaOH	NaOH + C	NaOH + Na_2O_2
After 1st fusion	0.145	0.14	0.10
After 2nd fusion	0.07	0.07	0.07
Total	0.22	0.21	0.17

This problem was not investigated further, because the method described here is intended for samples containing traces of tin, which are not likely to contain cassiterite.

SUMMARY

Procedures are given for the determination of traces of tin with dithiol (4-methyl-1,2-dimercaptobenzene) by visual color comparison and absorptiometric measurement, with special reference to silicate rocks, meteorites, and sulfides. The sensitivity is 1 p.p.m. Sn with 0.5 g of sample. Tin is separated by distillation of the bromide. Provision is made for the presence of selenium.

RÉSUMÉ

Des procédés sont décrits pour le dosage de traces d'étain, au moyen de dithiol (4-méthyl-1,2-dimercaptobenzène) par comparaison visuelle de la coloration et par mesures absorptiométriques, en particulier dans les silicates, les météorites et les sulfures. La sensibilité est de 1 p.p.m. d'étain pour des échantillons de 0.5 g. L'étain est séparé par distillation de son bromure. Des précautions doivent être prises en présence de sélénium.

ZUSAMMENFASSUNG

Es werden Verfahren beschrieben, um Spuren von Zinn mittels Dithiol (4-Methyl-1,2-dimercaptobenzol) durch visuellen Vergleich der Färbung und durch absorptiometrische Messungen besonders in Silikaten, Meteoriten und Sulfiden, zu bestimmen. Die Empfindlichkeit ist 1 p.p.m. Zinn für Einwaagen von 0.5 g. Das Zinn wird durch Destillation seines Bromids abgetrennt. Bei Gegenwart von Selenium werden spezielle Vorkehrungen getroffen.

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THE COLORIMETRIC DETERMINATION OF THORIUM USING 1-(o-ARSONOPHENYLAZO)-2-NAPHTHOL-3:6-DISULPHONIC ACID

by

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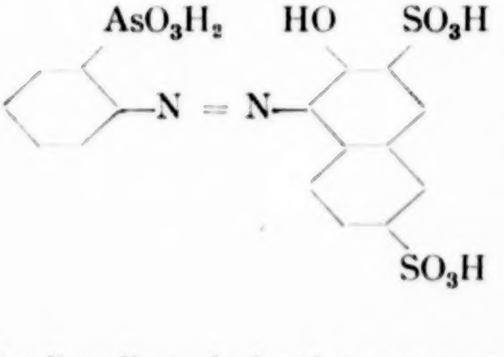
KUZNETSOV[1,2] in 1941 prepared 1-(o-arsonophenylazo)-2-naphthol-3:6-disulphonic acid and showed its reaction with thorium ions to form a specific red precipitate. At high dilution the precipitate dissolves and under certain specified conditions the method can be used for the colorimetric determination of thorium. From this work THOMASON, PERRY AND BYERLY[3] developed a method for the determination of thorium in microgram quantities and listed a few of the interferences that may be expected. This and later work[4] showed that 1-(o-arsonophenylazo)-2-naphthol-3:6-disulphonic acid is generally specific for quadrivalent ions. The present communication shows the further development of this work with a more detailed account of the interferences which may be commonly encountered in lanthanon analyses and indicates methods by which some of them may be overcome. Details are also given of the spectrophotometric determination of thorium in monazite.

Various trivial names have been proposed for the compound: Thoron, Thorin, Thoronol and Naphtharson. In this country APANS is customary and this is the name which will be used in this paper. All these refer to the same structural formula, which may be represented:



The dye in the form of its di-sodium derivative can now be obtained commercially in this country. Details for its preparation are, however, available[2,6,7].

EXPERIMENTAL

Aqueous APANS solutions containing thorium show an absorption peak at 545 mμ when compared with similar solutions not containing thorium. Spectrophotometric analyses of solutions prepared according to the technique of VOSBURGH AND COOPER[8] indicate that a complex is formed from one atom of thorium and two molecules of APANS. 1 mg of thorium ion was mixed with various amounts of 0.1% aqueous APANS solution, sufficient hydrochloric acid was added to give a final pH of 0.75 and the solutions were diluted to 100 ml with water. These solutions were compared on a spectrophotometer at 545 mμ with similar solutions containing no thorium. The absorption was found to be a maximum when 15 ml of 0.1% reagent were used. This amount was therefore employed for each determination.

100 ml of solution containing 15 ml of 0.1% APANS and various amounts of thorium from 0 to 1.2 mg were adjusted with hydrochloric acid to a pH of 0.75 and the optical densities of the solutions compared with similarly prepared solutions containing no thorium. A graph of "mg thorium" versus "optical density" gave a straight line when a Hilger "Uvispek" spectrophotometer was used at a wavelength of 545 mμ and slit width 0.2 mm. If the same solutions were compared on a Hilger Spekker absorptiometer using the mercury vapour lamp, Calorex heat filters and Ilford 605 filters, the combination recommended for selecting the mercury 546 mμ line, a curved graph was obtained. This flattened considerably above 1.0 mg thorium. The cause of the flattening was found to be due to the transmission of mercury yellow lines at 577 mμ and 579 mμ and this was prevented by inserting Wratten 77 filters together with the above combination. Due to the abnormal thickness of this combination the E-shaped filter container may have to be built out with a thin cardboard.

The graph obtained with this combination is a straight line and enables the drum reading to be converted to "mg thorium" by the use of a conversion factor.

Stability of colour

With pure thorium chloride solutions the complex has been found to be stable for over a month in the cold. If the solutions are heated above 35° C for any length of time decomposition sets in and anomalous results are obtained.

Increases of temperatures from 15° C to 25° C increase the absorption both of the blank and of the thorium-containing solution, when compared with water. The solution containing thorium has, however, a greater temperature coefficient than the blank, so that the net result is an increase in the measurements. A rise in temperature from 15° C to 25° C on a solution containing 0.95 mg thorium as chloride has been found to cause an increase of drum reading of 3.3%.

Effect of pH

The safe limits for acidity lie between pH values of 0.5 and 1.5. Acidities outside these limits cause considerable and sharp diminution of the colour. These limits correspond to an acidity of between 0.5 and 4.0 ml of concentrated hydrochloric acid (11.4*N*) per 100 ml.

METHOD

Reagents

0.1% APANS solution — Dissolve 1 g of 1-(*o*-arsonophenylazo)-2-naphthol-3:6-disulphonic acid (di-sodium salt, as supplied by B.D.H.) in water and dilute to 1 litre in a standard flask.

Diluted hydrochloric acid (1 + 4) — Dilute 200 ml of concentrated hydrochloric acid to 1 litre with water.

Hydroxylamine hydrochloride solution — Dissolve 10 g of hydroxylamine hydrochloride in 100 ml of water.

Phenolphthalein indicator — 1 g of phenolphthalein dissolved in 60 ml of industrial alcohol and 40 ml of water.

Diluted ammonia solution (1 + 1) — Dilute 50 ml of concentrated ammonia solution sp.gr. 0.88 to 100 ml with water.

All reagents should conform to recognized analytical standards.

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Apparatus

Hilger Spekker absorptiometer H760 fitted with a mercury vapour lamp and Wratten 77, Ilford 605 and Calorex filters.

Procedure

To the solution containing between 0 and 1.3 mg thorium in a 100 ml volumetric flask add two drops of phenolphthalein indicator and neutralize to a red colour with diluted ammonia solution (1 + 1). Add 10 ml of diluted hydrochloric acid (1 + 4), 5 ml of hydroxylamine hydrochloride solution and 15 ml of 0.1% APANS solution. Prepare a blank solution at the same time containing similar amounts of acid, hydroxylamine hydrochloride solution and APANS only. Make each solution up to the mark and immerse in a thermostat at 25° C for 15 minutes. Measure the solution in 1 cm cells with a Hilger Spekker absorptiometer using a mercury vapour lamp and Wratten 77, Ilford 605 and Calorex filters. Determine the amount of thorium present from solutions similarly prepared with known amounts of thorium.

A solution of pure thorium nitrate containing 0.952 mg thorium has been measured seventeen times by the addition of fresh additions of dye over a period of three months by the same person. An analysis of the results gave the mean drum reading for this solution to be 0.625 with a standard deviation of 0.003, an error of 0.5%.

Effect of interfering cations

The procedure given above was used in the presence of some common cations in order to determine their effect on the drum reading.

i) *Lanthanons.* The effect of adding increasing amounts of lanthanon ions has been investigated. Cerium^{III}, lanthanum, samarium and yttrium interfere by complexing with APANS, the amount of interference decreasing for a given weight of lanthanon in the order stated. Cerium^{IV} bleaches the colour and must be removed with hydroxylamine hydrochloride solution before addition of APANS. Lanthanons alone do not give a straight line graph under the conditions of the procedure except, perhaps, at amounts less than 50 mg of lanthanon. The drum readings are, however, too low to measure accurately within this range. The interference from all the lanthanons can be neglected except for the most accurate determinations if less than 5 mg of lanthanon ion is present.

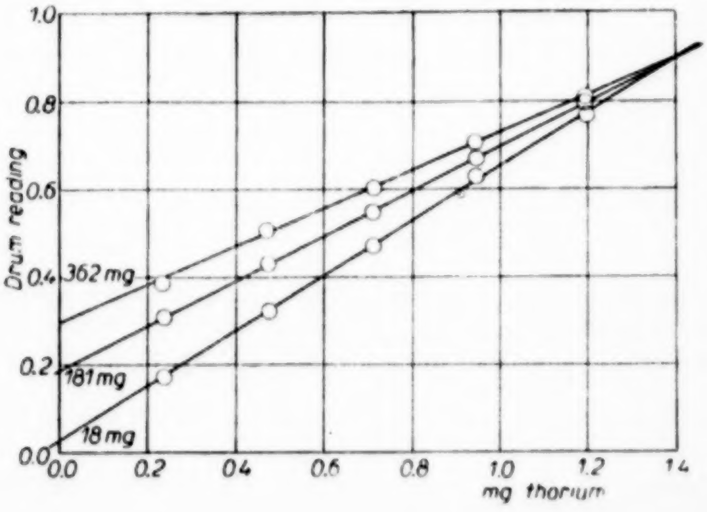

Fig. 1. Effect of mixed lanthanons from monazite (as oxides) on the drum readings of thorium solutions.

In the presence of constant amounts of lanthanon and varying amounts of thorium two effects are caused —

a) The slope of the graph is altered

b) A positive reading at zero thorium content is obtained.

The effect is shown graphically in **Fig.** 1.

ii) *Alkali-metals and ammonium.* The effect of lithium, sodium, potassium and ammonium as chlorides on the thorium-APANS complex has been investigated. Each ion causes diminution of the colour but the effect of lithium is considerably greater than the other three (Fig. 2). The effect of the ammonium ion is not recorded as it was considerably less than that of sodium ion.

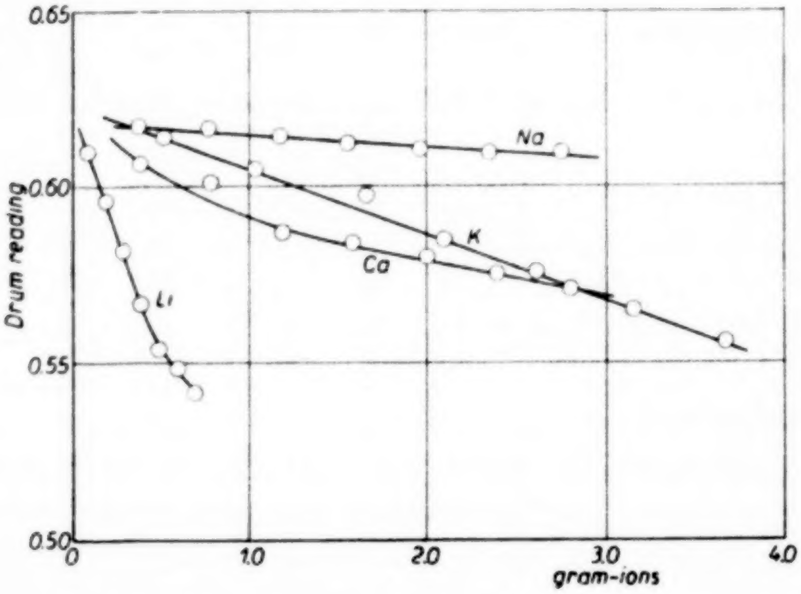

Fig. 2. Interference of lithium, sodium, potassium and calcium ions, on solutions containing 0.95 mg thorium.

iii) *Alkali-earths.* Calcium as chloride causes an interference similar to potassium (Fig. 2). Barium ions cause no interference up to a concentration of about 200 mg barium per 100 ml. At concentrations higher than this an orange-red precipitate appears. This may take as long as an hour to form.

iv) *Iron and aluminium.* A solution of ferric chloride causes considerable interference. The effect can be minimized by reducing the iron to the ferrous state by heating for 10 minutes with hydroxylamine hydrochloride solution. Heating is essential for the reduction to take place. Even under these conditions the effect of iron is considerable and its presence should be avoided wherever possible. The effect of both ferrous and ferric ions is shown graphically together with the effect of aluminium in Fig. 3.

v) *Tin and lead.* Both stannous and stannic chlorides cause strong interference and must be absent. Lead interferes in large amounts by the precipitation of its chloride. It may, however, be tolerated at amounts up to 125 mg lead per 100 ml under the conditions of the procedure before precipitation occurs.

vi) *Zirconium and titanium.* Zirconium forms a red precipitate with APANS which is more insoluble than the thorium complex; it should therefore be absent. The reagent has been used for the determination of zirconium[4]. Titanium interferes similarly.

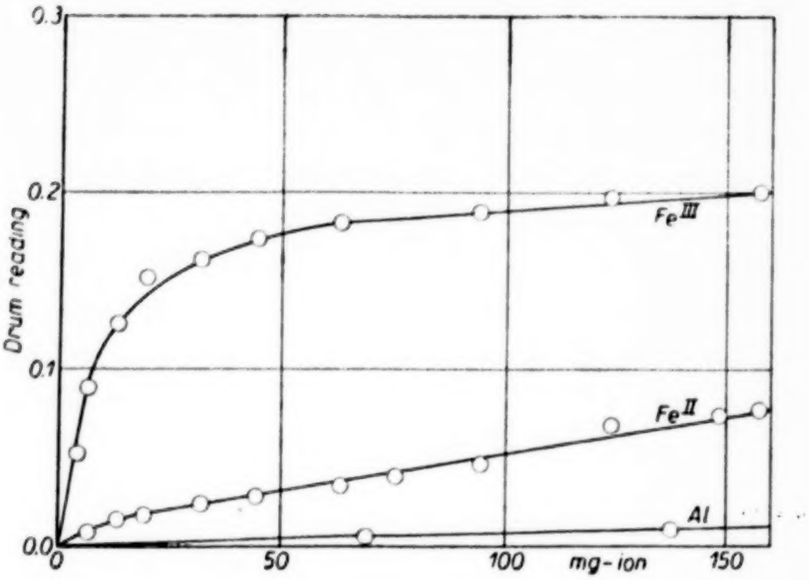

Fig. 3. Effect of ferrous, ferric and aluminium ions on APANS.

vii) *Uranium.* The influence of the uranium (UO_2^{+2}) ion on APANS has been investigated and interference is slight; at concentrations of about 50 mg uranium per 100 ml the effect is equivalent to about 0.2 mg thorium. The effect of uranium^{IV} has been reported previously[3]; it should be absent.

Effect of interfering anions

In general any anion which complexes thorium can be expected to interfere.

i) *Fluoride.* Fig. 4 shows the effect of fluoride on the drum reading of a thorium-APANS complex prepared by the standard procedure and containing 0.95 mg thorium.

The effect of small amounts of fluoride ion can be minimized and almost eliminated by the addition of aluminium ions. Fig. 4 shows that 0.95 mg thorium may be estimated in the presence of as much as 1 mg fluoride by the addition of 10 mg aluminium as the chloride or nitrate. This amount of aluminium is insufficient to cause interference on its own. The drum reading obtained under these conditions corresponds to 0.923 mg thorium, an error of less than 3%. In the absence of aluminium the optical density obtained would correspond to 0.457 mg thorium.

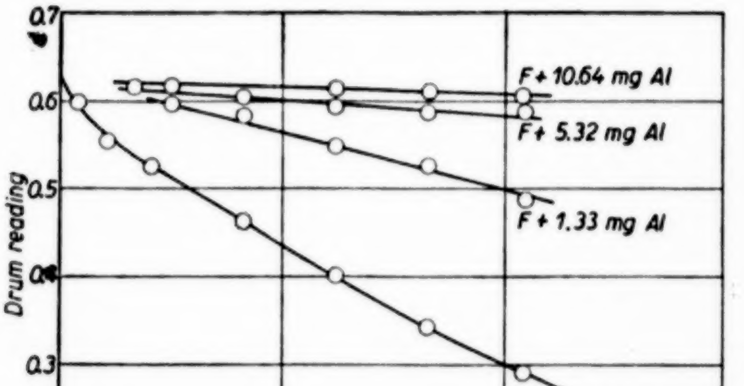

Fig. 4. Suppression of fluoride interference by aluminium ions. Thorium content = 0.95 mg.

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Attempts were made to remove fluoride ion in solutions containing 1 mg thorium and similar amounts of sodium fluoride by fuming with perchloric acid. This was not entirely successful and more consistent results were obtained by fuming with 0.1 g of boric acid as well. The results obtained after the determination of thorium by the standard procedure indicated that although the fluoride was expelled the final drum reading was slightly higher than expected. The experiments were therefore repeated without the addition of thorium and it was found that irrespective of the amount of sodium fluoride taken the drum reading remained the same (Table I).

TABLE I

FUMING OF SODIUM FLUORIDE WITH PERCHLORIC ACID AND BORIC ACID

mg NaF	0	0.4	1.6
Drum reading	0.016	0.015	0.015

Varying amounts of boric acid within the range 0–0.5 g had no effect upon the drum reading. It was therefore concluded that the discrepancies obtained were due entirely to the fuming of the perchloric acid.

The interference disappears if the solution is diluted to a volume and a sufficiently small aliquot taken for determination. An effect in the opposite direction was noticed by HORTON *et al.*[5], who used the interference of the thorium-APANS complex by fluoride ion for the determination of fluorine following a distillation from perchloric acid. He attributed the interference to undecomposed perchloric acid, but it has been noticed that unfumed perchloric acid, whether containing dissolved boric acid or not, does not interfere.

ii) *Sulphate and phosphate.* Phosphate and sulphate both interfere noticeably with the optical density of thorium-APANS complexes. The effect is shown graphically in Fig. 5.

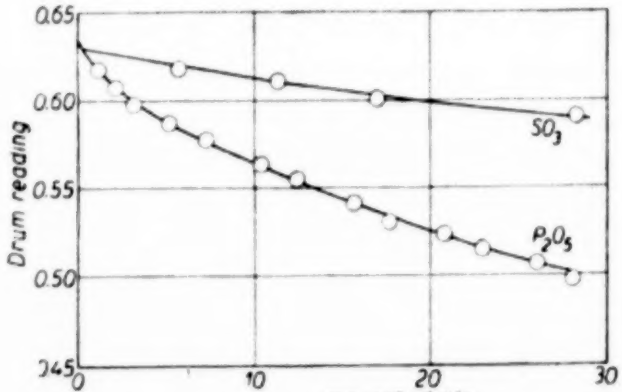

Fig. 5. Effect of phosphate and sulphate on a thorium-APANS complex containing 0.95 mg thorium.

iii) *Nitrate and chloride.* The effect of nitrate ion is extremely slight and for most purposes it can be neglected. About 1.5 g nitrate ion is required to decrease the drum reading by 1%. Chloride ion is completely without effect. However, solutions containing 10 g of sodium chloride have been found to contain a bright red precipitate after standing for twenty-four hours.

iv) *Sulphur dioxide and sulphites.* It has been found that solutions containing dissolved sulphur dioxide exhibit a red colour similar to that given by thorium ions. Consequently any anion such as sulphite or thiosulphate, which in the acid conditions of the procedure will give sulphur dioxide, can be expected to interfere. If the solutions are allowed to stand for a long period bleaching of the dye occurs and the solutions become colourless. Examination of the absorption of solutions containing sulphur dioxide show a wide absorption band with a peak at 532 mμ.

The interference can be removed by treating the solution before addition of APANS with neutral potassium permanganate solution until the purple colour persists. 0.5 g of hydroxylamine hydrochloride is then added and the procedure completed by the addition of acid and APANS.

v) *Carbon dioxide and carbonates.* Carbon dioxide gas present in the solution with thorium ions and APANS diminishes the red colour of the complex. If any substance which gives carbon dioxide under the conditions of the procedure is believed to be present the procedure should be followed as far as the addition of acid and then the solution should be boiled to expel carbon dioxide. The solution may then be cooled, APANS added, and the procedure completed.

vi) *Organic acids.* These normally interfere when present in large amounts. They may be removed by evaporation of the sample to near dryness with nitric acid with or without the addition of perchloric acid. If perchloric acid is used an aliquot of the final solution must be taken to avoid the interference effect of fumed perchloric acid.

DISCUSSION

It has not been possible to find a method which will separate thorium quantitatively from other interfering ions. In the past it has been thought that oxalate separation was quantitative in the presence of lanthanons which are co-precipitated. This view has recently been shown to be erroneous[9] and work carried out in these laboratories has confirmed these opinions. It has therefore been found advisable not to remove interfering ions by precipitation of thorium but to allow for their effect. If routine analysis for thorium is carried out in the presence of much interference it has been found simplest to determine the amount of interfering ion, increase it by the addition of a measured quantity of a standard solution to a definitely known amount, and use a conversion factor constructed under these conditions. This method has been successfully applied to the determination of thorium in solutions containing phosphate.

The amounts of interfering ions which separately will not interfere with the standard graph or conversion factor are given in Table II.

TABLE II

AMOUNT OF ION CHANGING THE DRUM READING OF 0.95 mg THORIUM BY 0.01

ion	Ce^{III}	Y	Li	Na	K	NH_4	Ca	Ba	Fe^{III}				
mg	6	16	60	2000	600	5000	180	200	0.5				
ion	Fe^{II}	Al	Sn^{II}	Sn^{IV}	Pb^{II}	Ti^{IV}	Zr	U^{VI}	P_2O_5	SO_3	F	NO_3	
mg	8.0	170	Nil	Nil	125	Nil	Nil	2	0.8	5	0.02	1500	

The determination of thorium in monazite

Experiments were performed on solutions of lanthanons containing thorium to determine the best method for precipitating thorium quantitatively. It has been found impossible to prevent losses occurring by any known method but conditions can be arrived at so as to make the loss a minimum.

The thorium losses on determination with oxalic acid appear to be due entirely to solubility and the use of paper pulp or close-textured filter papers appear to make little difference to the final result. The following method has been developed for the determination of thorium in monazite. Due to lanthanon ions being present in the final solution which is examined spectrophotometrically the "percentage thorium oxide" found is slightly high. This is offset by a thorium loss of about 0.5 mg in the separation with oxalic acid. The combination of these two factors means that the final result is about 0.05 high.

A 'synthetic' monazite has been prepared containing Pb, Fe, Al, U, P_2O_5, Ca, Ce and Th in the proportions present in South African monazite. Using the given method, duplicate determinations on two separate precipitations with oxalic acid gave 5.57, 5.55 and 5.51, 5.55% ThO_2. The true thorium content was equivalent to 5.49% ThO_2.

A South African monazite gave 5.40, 5.37 and 5.40, 5.39% ThO_2.

Results obtained by other methods were:

i) Two precipitations with oxalic acid and final determination by benzoic acid[10]
5.2, 4.8%

ii) Chromatographic method[11] using APANS for final determination
5.36, 5.32%

The monazite is opened with perchloric acid by a modification of the procedure recommended by WILLARD AND GORDON[12].

METHOD

Reagents

Perchloric acid — An approximately 70% w/v solution.
Concentrated hydrochloric acid — 11.4*N*.
Hydrazine hydrochloride — crystals.
Diluted hydrochloric acid (1 + 3) — Mix 80 ml concentrated hydrochloric acid with 240 ml water; this amount is required for each determination.
Diluted hydrochloric acid (1 + 4) — Dilute 200 ml 11.4*N* hydrochloric acid to 1 litre with water.
Bromphenol blue indicator — Dissolve 0.1 g in 250 ml of 20% v/v industrial alcohol.
Concentrated ammonia solution — sp.gr. 0.88.
Concentrated nitric acid — 16.0*N*.
Oxalic acid — crystalline.
Oxalic acid wash liquor — Dissolve 20 g of oxalic acid in water, add 10 ml of concentrated nitric acid and dilute to 1 litre.
All reagents should conform to recognized analytical standards.

Apparatus

250 ml conical flask with a B 29 ground glass socket and an air condenser about 40 cm long with a B 29 cone.

Procedure

Grind the sample so that it all passes through a 120 mesh sieve. Weigh 10 g and transfer to the 250 ml conical flask. Add 40 ml perchloric acid and boil under the reflux air condenser on a hot plate for 3 hours. Conditions should be arranged so that the perchloric acid refluxes about 10 cm below the top of the condenser. Cool carefully, remove the air condenser and add 100 ml of diluted hydrochloric acid (1 + 4). Add slowly with vigorous shaking 4 g hydrazine hydrochloride, then heat to boiling and keep hot for one hour.

Cool the flask under the tap, add three Whatman accelerators, or an equivalent amount of ashless floc, and shake until dispersed. Filter through a 1 cm paper pulp pad using suction. Wash thoroughly with diluted hydrochloric acid (1 + 3) using 200 ml in all. Wash pad twice with small amounts of water. Transfer filtrate to 500 ml flask using the remaining 120 ml of diluted hydrochloric acid (1 + 3) and dilute to the mark with water.

Pipette a 50 ml aliquot into a 250 ml beaker, add a few drops of bromphenol blue indicator and neutralize with concentrated ammonia solution added dropwise until the indicator turns blue. Add 3 ml concentrated nitric acid, stir and dilute to 100 ml. Heat to boiling and add gradually 5 g oxalic acid, stirring continuously. Stir for 2-3 minutes after the addition and allow to stand in a cold water bath for 1 hour or longer. Filter the precipitate on a 12.5 cm Whatman 540 paper and wash with oxalic acid wash liquor.

Transfer the paper and precipitate to the original 250 ml beaker. Add 30 ml concentrated nitric acid and 10 ml perchloric acid. Cover the beaker with a clock-glass and evaporate the contents until the vigorous end reaction has ceased and all traces of filter paper have vanished. Fume gently for 5 minutes. Cool the beaker and wash the contents quantitatively into a 500 ml standard flask. Make up to the mark with water.

Withdraw a 10 ml aliquot by means of a pipette and deliver into a 100 ml standard flask. Determine the thorium content by the procedure given on page 164 but omitting the neutralization to the red colour of phenolphthalein.

$$\begin{aligned}&\%\ \mathrm{ThO_2}\ \text{in monazite}\\ &= \frac{\text{mg ThO}_2}{1000} \times \frac{500}{10} \times 100\\ &= 5 \times \text{mg ThO}_2\end{aligned}$$

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SUMMARY

A method is described for the determination of thorium in milligram quantities using 1-(*o* arsonophenylazo)-2-naphthol-3:6-disulphonic acid (APANS) with a precision of 0.5%. An account of the interferences to be expected from some common ions is given and the method is employed in the determination of thorium in monazite following an oxalate separation.

RÉSUMÉ

Une méthode est décrite pour le dosage du thorium (pour des teneurs de l'ordre du mg) au moyen de l'acide 1-(*o*-arsonophénylazo)-2-naphtol-3:6-disulfonique (APANS), avec une précision de 0.5%. L'influence de certains ions courants est étudiée. Cette méthode est utilisée pour le dosage du thorium dans la monazite, après séparation comme oxalate.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben, um Thorium (in der Grössenordnung vom mg) mit Hilfe der 1-(*o*-Arsonophenylazo)-2-naphtol-3:6-disulphonsäure (APANS) mit einer Präzision von 0.5% zu bestimmen. Der Einfluss gewisser häufiger Ionen wurde untersucht. Diese Methode wird für die Bestimmung von Thorium im Monazit angewandt, nachdem es als Oxalat ausgeschieden worden ist.

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ÉTUDE DU DOSAGE DU PHOSPHORE ET DE L'ARSENIC DANS LES ACIERS PAR COLORIMÉTRIE

par

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I. OBJET DE L'ÉTUDE

1. Mettant à profit les propriétés des hétéropolyacides silico- et phosphomolybdiques, l'on a précédemment[1,2] étudié le dosage colorimétrique du silicium et du phosphore dans les aciers.

L'objet initial de la présente étude est la mise au point d'une méthode de dosage de l'arsenic fondée sur les propriétés parallèles des hétéropolyacides arséniomolybdiques.

2. Une propriété nouvelle découverte au cours de cette recherche, touchant la réduction des hétéropolyacides molybdiques a conduit à revenir sur la question du dosage du phosphore, déjà traitée précédemment.

3. En définitive, le présent travail donne des méthodes nouvelles pour le dosage colorimétrique du phosphore et de l'arsenic dans les aciers.

II. PARTIE BIBLIOGRAPHIQUE

4. S'agissant de doser l'arsenic à l'aide du complexe molybdique, le phosphore doit être séparé préalablement, car dans les milieux d'acidité convenant à la formation et à la réduction de l'acide arséniomolybdique, l'acide phosphomolybdique, qui serait également formé et réduit, donnerait sa coloration bleue propre, qui se superposerait ainsi à celle de l'arsénio-conjugué réduit.

Les techniques classiques prévoient donc la séparation par distillation de l'arsenic; aucun test ne permet cependant de s'assurer que l'arsenic a bien été distillé en totalité, si ce n'est évidemment de répéter à plusieurs reprises la détermination entière, distillation et dosage, et de juger de la réactitude des opérations par la concordance des résultats obtenus.

5. KAKITA[3] a fait connaître une méthode, selon laquelle l'acide phosphomolybdique est extrait sélectivement par l'alcool amylique.

Dans le milieu aqueux résultant de cette séparation, l'arsenic est dosé colorimétriquement au moyen de la coloration bleue du conjugué arséniomolybdique, réduit au moyen de l'hydrazine.

III. PARTIE EXPÉRIMENTALE

6. Il a paru désirable de faire usage, dans cette technique, de l'acide ascorbique, déjà utilisé antérieurement[2], et qui donne des colorations bleues beaucoup plus pures que l'hydrazine.

Bibliographie p. 182

Les exemples suivants, représentent l'aboutissement des investigations expérimentales poursuivies sur ce point.

Séparation du phosphore et dosage de l'arsenic en l'absence de fer.

Dans 5 béchers (50), distribuer:
10 ml de liqueur de phosphate disodique (1 ml = 10 γ P);
respectivement 0-1-2-3-4 ml de liqueur d'arséniate de sodium (1 ml = 25 γ As);
5 ml de liqueur 5*N* d'acide sulfurique;
respectivement 25-24-23-22-21 ml d'eau; enfin
10 ml de solution de molybdate de sodium (10 g/l) (L'acidité ainsi réalisée est 0.5*N* en acide sulfurique.)
Chauffer à 70-80° (b.m.) pendant 5 à 10 min. Laisser refroidir.
Extraire par un mélange de 75 parties en volumes d'éther et 25 parties d'alcool amylique (deux extractions avec 25 ml, une extraction avec 20 ml du mélange de solvants).

Les phases aqueuses étant reçues en fioles jaugées (100), distribuer successivement: eau q.s.p. 75 ml environ; 3 ml de liqueur 3*N* d'acide sulfurique, 10 ml de solution de molybdate de sodium (10 g/l), 10 ml de solution d'acide ascorbique (2 g/l), et de l'eau pour compléter à 100 ml environ. (L'acidité ainsi réalisée est 0.4*N* en acide sulfurique.)

Porter au bain-marie bouillant 10 min. Refroidir, compléter à 100 ml. Mesures photométriques (λ = 725 mμ). Les résultats sont consignés dans le Tableau I, colonne 1.

Gamme d'étalonnage

Dans 5 fioles jaugées (100), distribuer:
liqueur d'arséniate de sodium (1 ml = 25 γ As: 0-1-2-3-4 ml); 8 ml de liqueur 5*N* d'acide sulfurique; de l'eau pour diluer à 85 ml environ; 10 ml de solution de molybdate de sodium (10 g/l); 10 ml de solution d'acide ascorbique (2 g/l) (Acidité réalisée: 0.4*N* en acide sulfurique). Porter au bain-marie bouillant 10 min. Refroidir. Compléter à 100 ml; mesures photométriques. Les résultats sont consignés dans le Tableau I, colonne 2.

TABLEAU I

As	*Mesures photométriques*	
γ	*1*	*2*
100	92 → 100	91.5 → 100
75	74	75
50	49	49
25	24	24
0	0	0

Il y a bien identité, à l'approximation expérimentale près, des mesures de l'arsenic, directement et après extraction.

7. *Remarques.* a) Le choix de l'acidité 0.5*N* en acide sulfurique pour la formation des acides phospho- et arséniomolybdiques résulte d'une étude systématique de l'acidité.

b) D'essais dans lesquels ont été employés, pour l'extraction de l'acide phosphomolybdique, différents solvants: alcool amylique; alcool *iso*butylique et benzène (parties égales); acétate d'amyle et éther (parties égales); alcool butylique normal et chloroforme; 25 parties d'alcool amylique et 75 parties d'éther, c'est cette dernière formule qui s'est montrée la plus efficace pour l'extraction de l'acide phosphomolybdique.

c) Il a été constaté que, dans l'extraction par ce solvant, une partie notable du molybdate mis initialement en oeuvre en vue de la formation des acides phospho- et arséniomolybdiques, se trouve extraite, de sorte qu'il n'en subsiste plus suffisamment dans la phase aqueuse pour développer la coloration bleue du conjugué arséniomolybdique réduit: il faut donc ajouter de nouveau du molybdate de sodium à ce moment du dosage.

d) En présence de fer, celui-ci doit être réduit au stade ferreux, préalablement à la réduction de l'acide arséniomolybdique; afin de ne pas faire usage de quantités trop importantes d'acide ascorbique, une réduction préalable doit être faite, et, après essai du chlorhydrate d'hydroxylamine, de l'acide thiomalique, du trichlorure de titane et du sulfite de sodium, c'est ce dernier qui a été retenu.

8. *Essais en présence de fer.* 1 g de fer est attaqué* et le liquide d'attaque, complété à 250 ml. A cinq prises d'essai de 25 ml de ce liquide, ajouter: 10 ml de liqueur titrée de phosphate disodique (1 ml = 10 γ P) et respectivement 0-1-2-3-4 ml de liqueur titrée d'arséniate de sodium (1 ml = 25 γ As). Neutraliser par la lessive d'hydroxyde de sodium (400 g/l) (tournesol). Ajouter successivement:
5 ml de liqueur $5N$ d'acide sulfurique; 10 ml de solution de molybdate de sodium (10 g/l), et de l'eau pour compléter à 50 ml (l'acidité sulfurique réalisée est donc $0.5N$). Chauffer à 70-80° pendant 5 min (bain-marie). Refroidir.

Extraire en ampoules à décantation par le mélange: alcool amylique (25 parties) et éther (75 parties), soit deux extractions par 25 ml, une extraction par 20 ml. Recevoir les phases aqueuses en fioles jaugées de 100.

Distribuer: 5 ml de solution de molybdate de sodium (10 g/l), 3 ml de liqueur $5N$ d'acide sulfurique; 10 ml de solution de sulfite de sodium crist. (100 g/l). Repos 2 à 3 min; 10 ml de solution d'acide ascorbique (30 g/l). Agiter. Compléter à 100 ml avec de l'eau (acidité sulfurique réalisée: $0.4N$). Chauffer au bain-marie bouillant 10 min. Refroidir. Les résultats des mesures photométriques (Tableau II) sont en accord avec ceux du Tableau I.

TABLEAU II

As γ	*Mesures photométriques*
100	93 → 100
75	76
50	49
25	24
0	0

9. On remarque que les termes sans arsenic des gammes sont légèrement colorés en jaune-brun. (Il s'agit sans doute de composés de réduction molybdiques.)

10. *Réduction en présence de bismuth, de titane ou de zirconium.* Si l'on suppose que les sels de ces trois métaux, donnant des complexes phosphoriques, masqueraient ainsi cet acide vis-à-vis de la réaction ceruleo-molybdique, leur introduction permettrait d'éviter l'extraction préalable de l'acide phosphomolybdique; il resterait bien entendu à étudier l'action de ces sels sur l'acide arsénique.

On observe que, pour des doses suffisantes de sels de titane ou de zirconium, les ions arsénio- et phosphomolybdiques, et orthomolybdiques sont en fait réduits *à froid;* au contraire, en présence d'un sel de bismuth, les acides phospho- et arséniomolybdiques et paramolybdique, sont réduits *à froid,* l'acide orthomolybdique lui-même ne l'étant pas.

Il semble que ces faits n'aient pas été signalés jusqu'à présent.

11. Pour les expliquer, l'hypothèse peut être faite, que le bismuth formerait des

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* Attaque selon[2], et *Appendice I* du présent travail.

complexes phosphoriques ou arséniques analogues au molybdate $(MoO_4)_2Bi^-$*, le bismuth ainsi introduit dans la molécule ayant pour effet, en augmentant l'encombrement, de faciliter la réduction de l'ion molybdique. La même explication vaudrait si l'on suppose la formation de zirconimolybdates ou de molybdates de zirconium, et de complexes analogues du titane**.

12. L'action des sels de bismuth, de titane ou de zirconium est précisée par les observations expérimentales suivantes.

5 ml de solution d'acide phosphomolybdique (0.66 g/l d'acide phosphomolybdique; 1 ml = 10 γ P), en milieu d'acidité sulfurique 1.2*N* et en présence de 12.5 mg de bismuth (*cf.* APPENDICES) et d'acide ascorbique (10 mg), sont réduits *à froid* (dilution 50 ml).

Le paramolybdate d'ammonium (solution à 0.59 g/l, correspondant en Mo à celle d'acide phosphomolybdique), dans les mêmes conditions, est réduit *à froid*, plus énergiquement encore que l'acide phosphomolybdique lui-même.

Mais inversement, le molybdate de sodium (solution correspondant à 0.820 g/l), dans les mêmes conditions, n'est pas réduit.

En vue de la réduction des acides phospho- ou arséniomolybdiques, formés per action des acides phosphorique ou arsénique avec l'acide molybdique, des concentrations suffisantes de molybdate de sodium et d'acide ascorbique sont nécessaires. L'optimum est:

— pour le dosage du phosphore: acidité 1.2*N* en acide sulfurique; 10 ml de solution de molybdate de sodium (20 g/l), et 2 ml d'acide ascorbique (30 g/l) pour un volume total de 50 ml.

— pour le dosage de l'arsenic: acidité 0.5*N* pour la formation de l'acide phosphomolybdique; acidité 0.4*N* pour la formation et la réduction du conjugué arsénio-molybdique bleu réduit, avec 5 ml de solution de molybdate de sodium (10 g/l) et 10 ml de solution d'acide ascorbique (30 g/l), pour un volume total de 100 ml.

13. *Réduction du phospho-conjugué en présence de titane ou de zirconium.*

Liqueur de bismuth: *cf.* APPENDICES.

Liqueur de titane ou de zirconium (1 ml = 1 mg de Ti ou de Zr). La quantité pesée de TiO_2 ou de ZrO_2 est attaquée par fusion en creuset de platine par le sulfate acide de sodium, reprendre *à froid* par l'acide sulfurique 5*N*.

A 25 γ de P (2.5 ml de liqueur de phosphate disodique, APPENDICE 1) (cas du bismuth), ou à 50 γ P (cas du titane ou du zirconium) ajouter les quantités variables voulues de liqueurs acides (5*N* en acide sulfurique) de bismuth, de titane ou de zirconium, puis les volumes voulus de liqueur 5*N* d'acide sulfurique (volume total de liqueur de bismuth, de titane ou de zirconium et d'acide sulfurique 5*N* = 12 ml); puis 10 ml de solution de molybdate de sodium (20 g/l), 2 ml de solution d'acide ascorbique (30 g/l) et de l'eau pour compléter à 50 ml. (Acidité des milieux ainsi réalisés: 1.2*N*.)

Dans chaque série, des témoins sont faits, étant exempts de solution phosphorique, afin de vérifier qu'il n'existe aucune réduction du molybdate seul, en l'absence de phosphate.

Les résultats sont consignés dans le Tableau III, p. 176.

Le titane et le zirconium sont à éliminer, comme entraînant la réduction de l'acide molybdique seul; le bismuth doit être employé à dose suffisante pour donner une réduction complète à froid.

14. *Réduction de l'arsénio-conjugué en présence de bismuth, de titane ou de zirconium.* A 50 γ As (liqueur d'arséniate de sodium 1 ml = 25 γ As), ajouter les volumes voulus de solution de bismuth, de titane ou de zirconium, et les volumes voulus de liqueur 5*N* d'acide sulfurique (volume total des liqueurs de bismuth, de titane ou de zirconium, et d'acide sulfurique à 5*N* = 4 ml); puis 5 ml de solution de molybdate de sodium (10 g/l), 5 ml de solution d'acide ascorbique (30 g/l), et de l'eau pour compléter à 50 ml. (Acidité des milieux ainsi réalisés: 0.4*N* en acide sulfurique.) Dans chacun des cas, des témoins sont faits dans lesquels on n'ajoute pas de liqueur d'arséniate (en présence de bismuth, aucun de ces témoins ne donne de coloration avec le molybdate en l'absence d'arsenic). Les résultats sont consignés dans le Tableau IV, p. 177.

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* Traité de Pascal, XI, p. 62.

** *ibid.*, V, p. 739.

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TABLEAU III

Bi *mg*	*Mesures photométriques* $\gamma = 670$ *mμ* *1 h*	 *2 h*	 *4 h*
15	52	66.5	68.5
12.5	46	63.5	67.5
10	46	62.5	67.5
7.5	41	61.5	66.5
5	33.5	57.5	66
2.5	27.5	52.5	64.5
1.25	20	43.5	61.5
1	31	55	59
0.75	21.5	46	55
0.5	15	36	49.5
0.25	7	16.5	32.5
0.125	4	10.5	20
0.0625	4	8.5	16
0	3	6	13

Ti *mg*	*2 h* *Molybdate seul*	 *Molybdate + phosphate*	*4 h* *Molybdate seul*	 *Molybdate + phosphate*	*6 h* *Molybdate seul*	 *Molybdate + phosphate*
12	6.5	12	20	37.5	51.5	95
10	5.5	9.5	16	29.5	41	77
8	3.5	8.5	11	24.5	31	67
6	1	5	7	19.5	22	54
4	0	2.5	4.5	12	17	37
2	0	2	1	11	7	35

Zr *mg*	*3 h* *Molybdate seul*	 *Molybdate + phosphate*	*6 h* *Molybdate seul*	 *Molybdate + phosphate*	*8 h* *Molybdate seul*	 *Molybdate + phosphate*
12	3	13.5	8.5	39	12.5	58.5
10	2	12	6	34.5	9	50
8	2	10.5	5.5	30	7.5	43.5
6	1.5	8.5	4	25	5.5	37.5
4	1	8.5	2.5	25	3.5	35.5
2	0.5	7	1.5	22	2.5	30.5

15. En résumé, seul le bismuth ne donne pas la réaction colorée avec l'orthomolybdate de sodium. Le développement à froid de la coloration bleue des conjugués phosphorique et arsénique est accéléré par des concentrations croissantes en bismuth; c'est pourquoi il est prévu une dose suffisante de cet élément dans les dosages.

16. *Dosage du phosphore.* Le mode opératoire (APPENDICE I) résulte de l'étude antérieure[2] et tient compte des faits nouveaux: introduction de 15 mg de bismuth en milieu d'acidité sulfurique 1.2*N*.

L'extraction finale par l'alcool amylique rend la méthode applicable aux aciers de toutes nuances, les éléments d'alliage n'ayant alors plus d'influence sur la mesure colorimétrique, et la coloration parasite mentionnée § 9 se trouvant éliminée.

Mesures à 670 mμ (courbe 1, p. 178). La courbe pour P variant de 0 à 50 γ (densité optique = f(P)), est une droite.

17. *Dosage de l'arsenic.* Dans le mode opératoire (APPENDICE II) l'acidité sulfurique lors de la formation des acides phospho- et arséniomolybdiques est 0.5*N*; l'acidité

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sulfurique du milieu de la réduction de l'acide arséniomolybdique est 0.4*N*. L'extraction finale par l'alcool amylique est conservée.

Mesures photométriques à 725 mμ (courbe 2, p. 178). La courbe pour As variant de 0 à 100 γ (densité optique = *f* (As)), est une droite.

TABLEAU IV

Bi mg	*Mesures photométriques*					
	½ h	*1 h*	*1.30 h*	*2 h*	*2.30 h*	*15 h*
2	45.5		45		44.5	
1.5	43		43		42.5	
1	40.5	42	42.5	42.5	41.5	
0.75	36.5	41	42	41.5	40 5	
0.5	35.5	41	41.5	41.5		
0.375	34.5	41	41.5	41.5		
0.25	28.5	38.5	39	39		
0.125	27	37	37.5	37.5		38
0.09375	23.5	36	37.5			37.5
0.0625	18.5	31.5	35			36.5
0.0468	15.5	27.5	34			36
0.03125	11	21	28.5			37
0.0156	7	11.5	17			37.5
0.0075	3	5.5	8			35

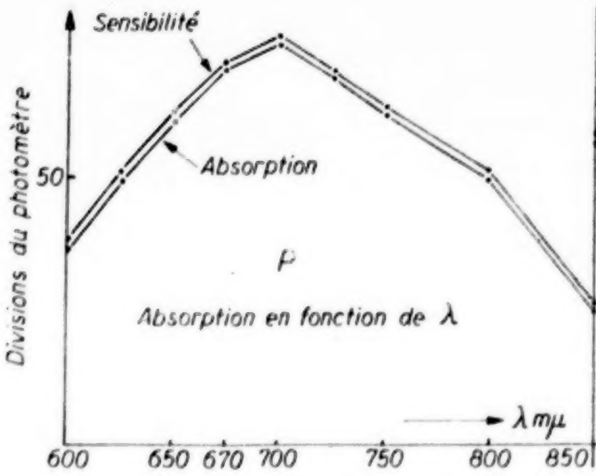
Ti mg	*2 h*		*4 h*		*5 h*	
	Molybdate seul	*Molybdate + arséniate*	*Molybdate seul*	*Molybdate + arséniate*	*Molybdate seul*	*Molybdate + arséniate*
4	30.5	30.5	38.5	49	40.5	55
3	25	23.5	29	39	30	43.5
2	13	15.5	17.5	25	18.5	28
1	7	7.5	8	11.5	8.5	13
0.5	4	4	4	7	4	7.5

Zr mg	*2 h*		*3 h*		*3.30 h*		*18 h*	
	Molybdate seul	*Molybdate + arséniate*	*Molybdate seul*	*Molybdate + arséniate*	*Molybdate seul*	*Molybdate + arséniate*	*Mo seul*	*Mo + arséniate*
4	9.5	23	10	32.5	10	36.5	11	47
3	6.5	21	7.5	29.5	7.5	33.5	8.5	47
2	4.5	14	5	20	5	23	6	41.5
1	3.5	8.5	4	12	3.5	13	4	38
0.5	2	5.5	2.5	8	2.5	9	4	33

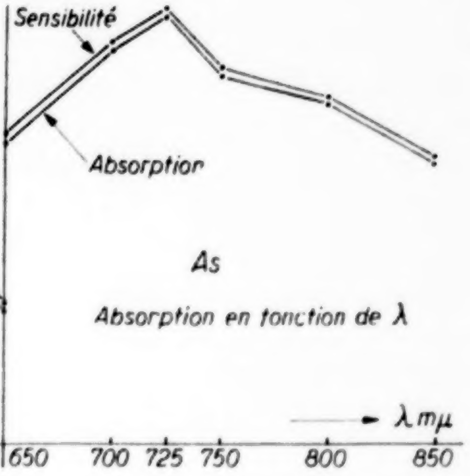
18. Pour justifier la séparation de l'acide phosphomolybdique de l'acide arséniomolybdique par extraction, selon le mode opératoire proposé APPENDICE II, il a été fait appel aux traceurs.

On introduit $^{76}_{33}$As (sous forme d'arséniate), en présence de phosphore (sous forme de phosphate), et l'on détermine l'activité de l'arsenic perdu et entraîné dans la phase organique, après précipitation, de celle-ci, de l'As* sous forme d'arséniate d'argent.

Liqueur de H_3AsO_4 marqué. Dissoudre 20 mg de $^{76}As_2O_3$ (à environ 10 mc par g, soit 0.2 mc) dans 2 ml de liqueur normale d'hydroxyde de sodium et 20 ml d'eau; ajouter 1 ml d'acide sulfurique (1.83) au demi, d'une liqueur de permanganate de



Courbe 1.



Courbe 2.

potassium *N*/50 jusqu'à coloration rose, puis 10 ml de liqueur de sel de Mohr *N*/50 et de nouveau de la liqueur permanganique jusqu'à coloration rose, enfin de la liqueur de sel de Mohr pour décolorer; compléter à 100 ml avec de l'eau (1 ml = 0.2 mg As_2O_3 = 2 μc).

Mode opératoire. Attaquer 1 g de fer pur (réduit par l'hydrogène) par 20 ml du mélange d'attaque perchlorique-nitrique-chlorhydrique (*cf.* APPENDICES), chauffer jusqu'à émission des vapeurs blanches perchloriques, reprendre par 50 ml d'eau, bouillir, transvaser en fiole jaugée de 250 ml, compléter à ce volume avec de l'eau. Dans un bécher de 50, recevoir 25 ml de ce liquide, Ajouter 100 γ de P (2 ml de liqueur de phosphate disodique à 0.580 g/l, dont 1 ml = 50 γ P),et 50 γ d'As (2 ml de liqueur d'arséniate disodique (12) APPENDICE II), puis 1 ml de liqueur As^{76}, soit 200 γ de ^{76}As.

Neutraliser par la solution de soude (400 g/l) (au bleu du tournesol). Ajouter: 5 ml de solution de bismuth (1 ml = 2.5 mg Bi; APPENDICE II (11)), 10 ml de solution de molybdate de sodium (10 g/l), et de l'eau pour compléter au volume de 50 ml environ. Porter au bain-marie (70-80°) pendant 5 min, refroidir.

Faire passer en ampoule à décantation, extraire deux fois avec 25 ml, puis une fois avec 20 ml du mélange de solvants (75 parties d'éther et 25 parties en volumes d'alcool amylique). Rejeter la phase aqueuse.

La phase organique, réunie en bécher (250), est portée au bain-marie pour évaporer l'éther. Ajouter 20 ml d'alcool éthylique, puis 2.5 mg d'As (5 ml de solution d'arséniate disodique à 2.08 g/l, dont 1 ml = 500 γ As); ajouter quelques gouttes d'indicateur bromo-thymol-bleu, puis goutte à goutte la liqueur *N* d'hydroxyde de sodium jusqu'à virage au bleu de l'indicateur, enfin 5 ml de solution de nitrate d'argent (100 g/l). Tiédir, laisser reposer. Filtrer sur creuset filtrant en verre fritté garni d'une rondelle de papier filtre. Laver avec un mélange de 15 ml d'alcool amylique, 20 ml d'alcool et 10 ml d'eau. Laisser sécher.

Gamme d'étalonnage. Dans deux béchers (100), distribuer 10 et 20 ml de liqueur d'^{76}As à 1 ml = 0.4 γ ^{76}As (Diluer 1 ml de la liqueur précédente à 1 ml = 0.000 2 g ^{76}As, à 500 ml avec de l'eau). Ajouter respectivement 5 ml de solution d'As à 1 ml = 500 γ As soit 2.5 mg d'As). Neutraliser par la liqueur *N* d'hydroxyde de sodium en présence de B.T.B. comme indicateur, ajouter 5 ml de solution de nitrate d'argent (100 g/l), tiédir, laisser reposer, filtrer et laver comme précédemment.

Chacun de ces deux témoins contient 4 et 8 γ ^{76}As, c'est-à-dire environ 0.04 et 0.08 μc d'activité.

Les activités des filtres, contenant les précipités d'arséniate d'argent, sont mesurées au compteur. Les résultats sont consignés dans le Tableau V.

TABLEAU V

^{76}As γ	*coups min.*
4	1 150 ± 35
8	2 460 ± 49
Essai	1 700 ± 41

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D'après celui-ci, il reste environ 5.5 γ de ^{76}As dans la phase organique, pour les 200 γ de ^{76}As mis en oeuvre: la perte en arsenic lors de l'élimination du phosphore par extraction au moyen du mélange alcool amylique — éther peut donc être évaluée à 2.5 à 3% de l'arsenic en oeuvre.

19. L'essai suivant a pour but de vérifier l'absence de phosphore dans la phase aqueuse, après extraction de celui-ci. On introduit du $^{32}_{15}$P (sous forme de phosphate), en présence de phosphate et d'arséniate non radioactifs, et l'on détermine l'activité de la solution aqueuse après extraction, le phosphore radioactif étant précipité sous forme de phosphomolybdate d'ammonium.

Liqueur de ^{32}P. a) 0.5 ml de solution radioactive de phosphate monosodique (à 1 ml = 2 mc, soit 1 mc) sont dilués à 100 ml (1 ml = 10 μc).

b) 1 ml de cette dilution est diluée à 500 ml (5 ml = 1 μc).

Mode opératoire. a) A 25 ml de la solution d'attaque de fer (§ 18, attaque de 1 g de fer, dilution à 250 ml), reçus en bécher (50), ajouter 0.1 mg P (2 ml de liqueur de phosphate disodique à 0.580 g/l, dont 1 ml = 50 γ P) et 50 γ As (2 ml de liqueur d'arséniate disodique (12) APPENDICE II), puis 5 ml de liqueur b) de ^{32}P (soit 1 μc).

Neutraliser par la solution d'hydroxyde de sodium (400 g/l) en présence de tournesol comme indicateur. Ajouter: 5 ml de solution de bismuth (1 ml = 2.5 mg Bi, APPENDICE II (11)), 10 ml de solution de molybdate de sodium (10 g/l) et de l'eau pour compléter au volume de 50 ml environ. Porter au bain-marie (70 à 80°) pendant 5 min, refroidir.

b) Extraire en ampoule à décantation deux fois par 25 ml et une fois avec 20 ml du mélange de solvants (75 vol. d'éther et 25 vol. d'alcool amylique). La phase organique est à rejeter.

c) A la phase aqueuse, ajouter 1 mg de P (2 ml de solution de phosphate disodique à 5.8 g/l, dont 1 ml = 500 γ P), chauffer à 70-80° au bain-marie, ajouter 2 ml de solution d'acide tartrique (500 g/l) et 40 ml de réactif nitro-tartrique-molybdique*. Chauffer à 80-85° pendant 5 min au bain-marie. Laisser déposer, filtrer sur creuset de verre fritté garni d'une rondelle de papier filtre.

Laver au moyen d'une solution nitrique-tartrique de nitrate d'ammonium (Neutraliser de l'ammoniaque (0.925) par de l'acide nitrique (1.33) et en ajouter après neutralisation 1/20 du volume total; diluer au cinquième et ajouter 0.5 g d'acide tartrique).

Gamme d'étalonnage. Diluer 5 ml de liqueur b) de ^{32}P à 500 ml (10 ml = 0.02 μc) (liqueur c).
Dans quatre béchers (100), distribuer:
40-30-20-10 ml de liqueur c de ^{32}P, dont l'activité est:
0.08-0.06-0.04-0.02 μc.

Ajouter 1000 γ P (2 ml de solution de phosphate disodique à 5.80 g/l dont 1 ml = 500 γ P) et opérer selon le mode opératoire (§ c) pour la précipitation.

Les résultats sont consignés dans le Tableau VI. Il résulte de celui-ci qu'il reste dans la phase aqueuse environ 0.03 μc sur 1 μc mis en oeuvre, soit 3 à 4% du phosphore initialement introduit. A remarquer que cette quantité est précisément du même ordre de grandeur que la perte en arsenic (§ 18); ces deux quantités s'équivalent.

La précision de la méthode, d'après ces résultats, peut se chiffrer par $< \pm 2\%$ du chiffre d'arsenic trouvé.

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* Réactif nitro-tartrique-molybdique.

a) Solution de paramolybdate d'ammonium: dissoudre 90 g de ce sel dans 550 ml d'ammoniaque (0.925).

b) Solution nitrique: dissoudre 35 g d'acide tartrique dans 100 ml d'eau et mélanger avec 770 ml d'acide nitrique (1.33).

Le réactif est obtenu en versant la solution a) dans b) et refroidissant; ajouter 0.025 g de phosphate diammonique dissous dans un peu d'eau. Agiter, porter à 80-85° et laisser déposer un jour avant l'emploi.

TABLEAU VI

^{32}P *μc*	*coups min.*
0.08	2 280 ± 50
0.06	1 896 ± 45
0.04	1 330 ± 37
0.02	520 ± 32
Essai	980 ± 30 : 0.03 μc

20. *Résultats analytiques.* Les résultats suivants ont été obtenus dans l'analyse des différents aciers (Tableau VII, les colonnes marquées d'un astérisque comprennent les chiffres obtenus par les méthodes décrites en APPENDICE).

TABLEAU VII

Repère	*C*	*S*	*Mn*	*Si*	*Ni*	*Cu*	*Cr*	*P*	*As*	*P**	*As**
1	0.307	0.012	0.503	0.287	0.171	0.164	0.040	0.009	0.046	0.0095	0.045
2	0.234	0.015	0.602	0.276	0.118	0.138	0.050	0.009	0.0497	0.009	0.0505
3	0.17	0.028	0.337	0.113	0.093	0.27	0.049	0.005	0.047	0.0055	0.044
4	0.7	0.025	0.468	0.27	0.134	0.27	0.1	0.033	0.035	0.0315	0.041

APPENDICE I

Dosage colorimétrique du phosphore dans les aciers

Principe — **Formation, à la température ordinaire, du dérivé phosphomolybdique bleu réduit.**

Réactifs particuliers

1 — Liqueur d'attaque: acide perchlorique (d = 1.61): 75 ml, acide nitrique (d = 1.33): 55 ml; acide chlorhydrique (d = 1.18): 20 ml.
2 — Solution de métabisulfite de sodium (sec R.P.): 200 g/l.
3 — Solution d'hydroxyde de sodium (400 g/l)
4 — Solution de molybdate de sodium (20 g/l)
5 — Solution d'acide ascorbique (30 g/l)
6 — Liqueur de bismuth. Dissoudre 1.440 g de BiO_2 par 50 ml d'acide sulfurique (1.83) au $^1/_2$, chauffer jusqu'à obtention d'un liquide limpide. Refroidir. Ajouter 115 ml d'acide sulfurique (1.83). Diluer au litre avec de l'eau.

Autre mode de préparation. Dissoudre 2.1 g de sulfate de bismuth, *à froid* dans de la liqueur 5*N* d'acide sulfurique; compléter au litre avec cette dernière liqueur sulfurique.

La liqueur de bismuth contient 1.25 mg Bi par ml, et son acidité est 5*N* en acide sulfurique.

7 — Liqueur de phosphate disodique: 0.116 g/l (1 ml = 10 γ P).

Mode opératoire

Prise d'essai: 1 g.

1) Attaque par 20 ml du mélange acide (réactif 1) (et 10 ml d'acide chlorhydrique (1.18) dans le cas des aciers inoxydables). Evaporer jusqu'à départ des vapeurs blanches perchloriques. Après refroidissement, reprendre par 30 ml d'eau, porter à l'ébullition. Refroidir. Compléter à 100 ml en fiole jaugée (100).

2) Après avoir filtré s'il y a lieu pour séparer la silice, prélever 10 ml du liquide, que l'on reçoit en bécher (100).

3) Ajouter 10 ml de solution de métabisulfate (réactif 2). Porter à l'ébullition 1 minute (sans dépasser ce temps). Refroidir.

Neutraliser par la solution d'hydroxyde de sodium (réactif 3) jusqu'à précipitation complète du fer (soit 1 ml environ). Ajouter immédiatement 12 ml de solution de bismuth (réactif 6): le précipité d'hydroxyde de fer est entièrement dissous.

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4) Ajouter 10 ml de solution de molybdate de sodium (réactif 4), agiter, ajouter 2 ml de solution d'acide ascorbique (réactif 5), agiter, et 4 à 6 ml d'eau. Agiter. Repos 30 min.

5) Faire passer en ampoule à décantation, et extraire une seule fois, par 45 ml d'alcool amylique, en rinçant le bécher avec celui-ci. Recevoir la phase alcoolique en fiole jaugée (50) et compléter à 50 ml avec de l'alcool amylique.

6) *Témoin*

20 ml de liqueur d'attaque (réactif 1) sont évaporés jusqu'à départ des vapeurs blanches perchloriques, reprendre par 30 ml d'eau et compléter à 100 ml avec de l'eau, en fiole jaugée. De ce liquide, prélever 10 ml et continuer selon opér. 3 et suivantes.

7) *Gamme d'étalonnage*

Prise d'essai: 1 g de fer pur (réduit par l'hydrogène)
Attaquer selon opér. 1.
En oper. 2, prélever 6 fois 10 ml que l'on reçoit dans 6 béchers (100).
A chaque prise d'essai ajouter respectivement:
0 — 1 — 2 — 3 — 4 — 5 ml de liqueur phosphorique (réactif 7);
Chaque terme de la gamme correspond donc à:
0 — 0.01 — 0.02 — 0.03 — 0.04 — 0.05% P de l'acier.
Opérer selon opér. 3 et suivantes.

8) *Mesures photométriques*

$\lambda = 670$ mμ. Mesurer la gamme par rapport au terme 0 de celle-ci:
Mesurer chacun des essais par rapport à son témoin.

9) *Calcul*

Le terme 5 de la gamme correspond à 100 divisions du photomètre, soit *n* divisions lues dans la mesure d'un essai considéré.

$$P\% = \frac{5\,n}{10.000}$$

APPENDICE II

Dosage colorimétrique de l'arsenic dans les aciers

Principe. Formation des acides phospho- et arséniomolybdiques; extraction de l'acide phosphomolybdique par le mélange éther-alcool amylique. Dans la solution aqueuse, formation à la température ordinaire du dérivé arséniomolybdique bleu réduit.

Réactifs particuliers

Les mêmes que pour le dosage du phosphore; en outre:
8 — Solution de sulfite de sodium crist. (100 g/l)
9 — Solution de molybdate de sodium (10 g/l)
10 — Solvant: 750 parties en volumes d'éther-oxyde d'éthyle et 250 parties en volumes d'alcool amylique.
11 — Liqueur de bismuth (1 ml = 2.5 mg Bi dans l'acide sulfurique 5*N*) préparée selon (6) à l'aide de 2.883 g de BiO_2, ou 4.2 g de sulfate de bismuth.
12 — Liqueur d'arséniate de sodium crist. à 0.104 g/l (1 ml = 25 γ As).

Mode opératoire

Prise d'essai 1 g.

1) Attaque par 20 ml de liqueur d'attaque (réactif 1). Evaporer jusqu'à départ des vapeurs blanches perchloriques. Après refroidissement, reprendre par 50 ml d'eau, porter à l'ébullition. Refroidir. Filtrer pour séparer la silice, laver à l'eau chaude. Compléter à 250 ml avec de l'eau.

2) Prélever 25 ml de ce liquide, recevoir en bécher (50). Neutraliser par la solution de soude (400 g/l) (réactif 3) jusqu'à virage au bleu du tournesol.

Ajouter 5 ml de liqueur de bismuth (réactif 11) (le fer précipité à l'état d'hydroxyde est entièrement redissous); 100 ml de solution de molybdate de sodium (10 g/l) (réactif 9) et 6 à 8 ml d'eau. Porter au bain-marie (température des liquides 70 à 80°) pendant 5 min. Refroidir.

3) Faire passer en ampoule à décantation. En lavant le bécher avec 25 ml du mélange de solvants (réactif 10), verser le tout dans l'ampoule à décantation. Agiter, extraire. Répéter l'extraction avec 25 ml du mélange de solvants, puis une troisième fois avec 20 ml.

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Recevoir les phases aqueuses en bécher (100). La phase organique est à rejeter*.

4) Ajouter en agitant après chaque addition: 5 ml de solution de molybdate de sodium (réactif 9); 3 ml de liqueur de bismuth (réactif 11); 10 ml de solution de sulfite de sodium (réactif 8). Repos 2 à 3 min. Ajouter 10 ml de solution d'acide ascorbique (réactif 5) et 20 ml d'eau. Agiter. Laisser reposer 25 à 30 min. La coloration bleue se développe.

5) Faire passer le liquide en ampoule à décantation; laver le bécher par 45 ml d'alcool amylique que l'on reçoit dans l'ampoule à décantation. Agiter, extraire en recevant la phase organique en fiole jaugée de 50 ml. Compléter à ce volume au moyen d'alcool amylique.

6) *Gamme d'étalonnage*

Prise d'essai: 1 g de fer pur (réduit par l'hydrogène).
Attaque par 20 ml de liqueur d'attaque (réactif 1) et opérer selon opér. 1.
Compléter finalement à 250 ml.
Prélever cinq fois 25 ml de ce liquide, recevoir dans 5 béchers (50).
Ajouter respectivement:
0 — 1 — 2 — 3 — 4 ml de liqueur d'arsenic (réactif 12).
Chaque terme de la gamme correspond donc à:
0 — 0.025 — 0.050 — 0.075 — 0.1% As de l'acier
Opérer selon opér. 2 et suivantes.

7) *Mesures photométriques*

$\lambda = 725$ mμ. Mesurer la gamme et les essais par rapport au terme 0 de la gamme.

8) *Calcul*

Le terme 4 de la gamme correspondant à la division 100 du photomètre, soit *n* divisions lues dans la mesure d'un essai considéré:

$$\text{As }\% = \frac{n}{1.000}$$

Précision ± 2% environ.

RÉSUMÉ

Les acides phosphomolybdique et arséniomolybdique se forment et sont réduits en dérivés de réduction bleus correspondants, dès la température ordinaire, en présence de certains ions métalliques: bismuth, zirconium, titane. Parmi ces ions, les deux derniers catalysent la réduction de l'acide molybdique dans les conditions d'acidité propices à la réduction des seuls acides phospho- et arséniomolybdiques. Le bismuth ne donne pas lieu à cette dernière réaction. Il a été choisi en vue des applications analytiques. Celles-ci concernent le dosage du phosphore et de l'arsenic dans les aciers. Les modes opératoires proposés sont donnés en appendice.

SUMMARY

Phosphomolybdic and arsenomolybdic acids are formed and reduced to their blue reduction products at normal temperature in the presence of certain metallic ions: bismuth, zirconium, titanium. Of these ions, the last two catalyse the reduction of molybdic acid under acid conditions favourable to the reduction of phospho- and arsenomolybdic acids. Bismuth does not bring about this last reaction. It was chosen because of its analytical applications, which are related to the estimation of phosphorus and arsenic in steels. The working methods proposed are given in an appendix.

ZUSAMMENFASSUNG

Die Phosphormolybdän- und Arsenmolybdänsäure werden gebildet und zu ihren blauen Reduktionsprodukten reduziert u.zw., beginnend bei Zimmertemperatur, in Gegenwart von gewissen Metallionen: Wismuth, Zirkonium, Titan. Von diesen Ionen katalysieren die zwei letzten die Reduktion der Molybdänsäure unter den für die Reduktion der Phosphor- und Arsenmolybdänsäure geeigneten Säurebedingungen. Wismuth löst die genannte Reaktion nicht aus. Es wurde für analytische Anwendungen gebraucht. Diese betreffen die Bestimmung des Phosphors und des Arsens in Stahl. Die vorgeschlagenen Arbeitsvorschriften werden im Anhang gegeben.

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* Elle sera récupérée par distillation fractionnée.

THE SPECTROCHEMICAL DETERMINATION OF INDIUM IN CASSITERITE

by

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In an investigation of the geochemical association of indium and tin, it was found necessary to develop a quantitative spectrochemical method for the determination of the indium content of cassiterite specimens. Since major interest was taken in specimens containing greater than 0.001% In, it was not necessary to employ a special procedure to give high sensitivity, such as the double arc method used by SHAW[1] or the chemical enrichment procedure of PROKOPENKO[2]. A fairly simple method using the cathode layer carbon arc has therefore been developed.

According to HARRISON[3] the most sensitive indium lines in the arc are 3039.4 Å (1000), 3256.1 Å (1500), 4104.8 Å (2000) and 4511.3 Å (5000), the numbers in brackets being an indication of the line intensities. Previous workers have generally used In 4511.3 Å or In 3256.1 Å as the analysis line for the determination of indium in mineralogical materials (AHRENS[4]). The use of either of these two lines in the present case was marred by possible interference from Ta 4511.0 Å and Mn 3251.6 Å, since traces of both tantalum and manganese have been present in some of the cassiterite specimens investigated. Although a correction for the manganese interference of In 3256.1 Å can be made (AHRENS and LIEBENBERG[5]) it was regarded as preferable to use In 3039.4 Å as the analysis line. The main possible interfering line in this case is Ge 3039.1 Å. However, since no germanium lines could be detected in any of the cassiterite specimens studied, use ot In 3039.4 Å for the determination of indium was regarded as satisfactory.

In order to obtain accuracy and precision, it was necessary to select a suitable internal standard. Since tin in cassiterite has fairly similar volatility and 1st ionization potential to indium, and because its use avoids the addition of an internal standard and possible accompanying errors due to dry mixing, it was decided to employ tin as an internal standard. The line Sn 3032 8 Å was eventually selected with In 3039.4 Å for the analysis pair.

EXPERIMENTAL

All determinations were made using a large Hilger Littrow spectrograph, with quartz optics. Electrodes were made from pieces of 6.5 mm diameter pure graphite rod. The lower cathode electrodes were similarly shaped to those generally employed in cathode layer work, being drilled with a cavity 1/16 in diameter and 4 mm deep. The upper anodes were similar to the cathodes but were undrilled. The optical conditions were such that an intermediate image of the arc was produced on a diaphragm which passed only light from the cathode layer region, this was focused at the collimator by means of a spherical lens near the slit. A 7-step rotating sector was mounted immediately before the slit. A D.C. arc discharge (110 volts on open circuit) carrying a current of 6 amp excited the powdered specimens, and exposures were of 90 sec in each case. Spectra were recorded on Ilford S.R. Panchromatic plates which were developed at 18° C according to directions from the manufacturers.

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Standard mixtures containing 1, 0.1, 0.03162, 0.01 and 0.001 % In were made by thoroughly dry mixing in an agate mortar pure In_2O_3 and SnO_2 in which no indium could be detected. In order to obtain plate calibration and a working curve, a self calibrating procedure was used (AHRENS[4] p. 136). Blackening curves (log-log plots of per cent transmission against relative exposure) of the analysis and internal standard lines and their backgrounds were prepared for the standard mixtures using the step sector and a Hilger non recording microphotometer. The values of the intensities of the lines, obtained from these curves by using a reverse abscissa scale at constant density, were corrected for background, and the ratios of the corrected intensities of the analysis pair were then plotted against per cent indium content on log-log coordinates to give the working curve, Fig. 1. Blackening curves for cassiterite specimens were obtained in the same manner as for the standard mixtures, and from the intensity ratio of the line pair the indium contents could be read from the working curve.

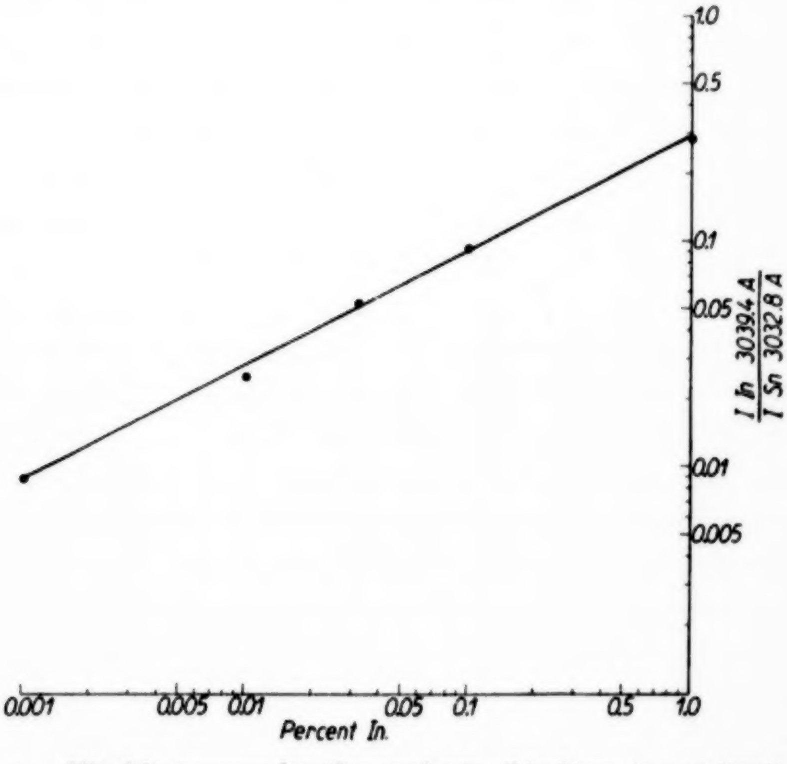

Fig. 1. Working curve for the analysis of indium in cassiterite.

REPRODUCIBILITY AND SENSITIVITY

In the analysis of cassiterite samples the standard deviation incurred was of the order of 5%.

The line In 3039.4 Å was just detectable at a concentration of 0.0001%.

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SUMMARY

In order to determine the indium content of cassiterite specimens, a spectrochemical method, using tin as internal standard and the cathode-layer carbon arc, has been employed. The precision of the procedure is approximately 5 %.

RÉSUMÉ

Une méthode spectrochimique (à arc), utilisant l'étain comme étalon interne, et des électrodes de graphite, est proposée pour le dosage de l'indium dans des échantillons de cassitérite. La précision est d'environ 5%.

ZUSAMMENFASSUNG

Es wird eine spektrochemische Methode (Bogenspektren) vorgeschlagen, welche Zinn zum internen Vergleich und Graphitelektroden verwendet, um Indium in cassiterithaltigen Substanzen zu bestimmen. Die Präzision ist ungefähr 5%.

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THE HETEROMETRIC MICRODETERMINATION OF SULFURIC ACID AS BARIUM SULFATE. A GENERAL STUDY

by

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INTRODUCTION

The determination of sulfuric acid by precipitation as barium sulfate is a reaction which has been most extensively studied in the past. Although no better method is known for the determination of sulfuric acid, this method has many disadvantages. The solubility product of barium sulfate is $1.0 \cdot 10^{-10}$. Its solubility is increased in strong acid solution and the determination must be carried out gravimetrically. If precipitated from a solution which contains other electrolytes the danger exists of interference by adsorption.

The adsorption phenomena in connection with barium sulfate have been studied extensively and are classics in this field. Since in heterometry[1,2] we have very rarely experienced interference by adsorption, we were interested in studying the case of barium sulfate and establishing the extent of interference by adsorption in this reaction. In the course of this study various phenomena occurred which seemed to us to be very instructive. Many experiments, although having no direct bearing on the immediate analytical aspect, were carried out in order to obtain a deeper insight into the phenomena.

From the material presented it is apparent that the heterometric determination of sulfuric acid proceeds quickly if carried out under appropriate conditions. Generally the end-point of the titration could be fixed without difficulty and the error was 0-3%. In almost all cases, after the first maximum density point, an exactly horizontal optical density line was obtained with no further change of density on the addition of excesses of titrant (= barium nitrate). This is so even in many cases where interference, which may be caused by adsorption, does occur. This interference is expressed by a displacement of the end-point of the titration, which appears either too early or too late, depending on whether the interference is caused by the cation or the anion of the supplement.

Generally it may be said that interference by adsorption was established by us only in particular cases, *i.e.* in the presence of excess of K^+, Fe^{+3}, NO_3^- or PO_4^{-3}, and then only if the concentration of the interfering cation or anion was many times greater than the molar concentration of the sulfuric acid which was determined. No interference was encountered in the presence of various bivalent cations at a concentration of $0.1M$ when the concentration of the sulfuric acid was $0.006M$; this means at a molar ratio of 16.6 : 1.

The difference in the behaviour of K^+ and NH_4^+ is remarkable. In the presence of the latter, no interference was observed. In contrast to $FeCl_3$, the presence of $0.1 M$ $AlCl_3$ did not interfere. In all cases with interfering ions, no interference occurred if the concentration of the ion was below $0.02 M$.

As far as the working conditions are concerned, the following may be said. When dilute aqueous sulfuric acid alone is titrated with barium nitrate, the heterometric titration becomes impossible as the sediment accumulates locally and no analytical end-point is obtained. It was found that a minimum amount of ethyl alcohol changes the titrating conditions entirely: the titration runs smoothly and a sharp end-point is obtained. A titration may thus be completed in ten minutes. If hydrochloric acid is present, the optimum amount of alcohol to be present is 15%-20%. The maximum optical density then decreases with the further increase of the alcohol concentration. The greater the amount of alcohol present, the greater the amount of hydrochloric acid which has to be added in order to work at optimum conditions. The influences of alcohol and hydrochloric acid work in opposite directions and identical results may be obtained with different alcoholic solutions under appropriate acid conditions.

One disadvantage which is common to most of the pure inorganic heterometric determinations is the relatively low sensitivity of the reaction. In this case, the lower limit of concentration of sulfuric acid which can be successfully titrated is $1\text{-}2 \cdot 10^{-3} M$. Using organic reagents such as α-nitroso-β-naphtol or dimethylglyoxime[3], a salt solution which is at least ten times more dilute may easily be titrated heterometrically with precision.

EXPERIMENTAL

The same apparatus was used and the same working conditions observed as in previous heterometric investigations[1-3]. In special cases only coloured filters were used in the presence of solutions which contained coloured foreign salts. In all experiments without exception, where an alcoholic solution was used, the percentage of alcohol (per volume) of the titrated solution and the titrant was always the same.

The temperature of the reacting solutions were thermostatically controlled at 20° C during all the heterometric titrations. This was done only to ensure that the experiments were carried out under similar working conditions, as temperature control is generally unnecessary when working at room temperature. The velocity of stirring was the maximum consistent with stable measurements and was controlled electronically, being more or less uniform in all experiments.

The reagents used were either analytical reagent or chemically pure. Ordinary distilled alcohol was used throughout this investigation. The total volume of the solution was 10 ml at the beginning of each experiment. In all experiments, without exception, the precipitation of barium sulfate began almost immediately upon the addition of the first drop of the titrant.

In most cases the analytical end-point of the titration was fixed directly by the intersection of a line drawn through the points of the last part (= last quarter) of the titration curve with the horizontal maximum density line. In some cases, *i.e.* in the presence of interfering supplements salts or acids, the location of the end-point became less sure (it was difficult to decide whether the above intersection point or the first contact point of the curve with the horizontal line had to be chosen). The value given in the Table is then only an approximation and is designated by an asterisk. In even less certain cases a question mark is placed after the value.

RESULTS AND CONCLUSIONS

a. *Influence of the medium*

It has already been mentioned that working in alcohol-water mixtures yielded better results than working in pure water solutions. In the latter case, the optical

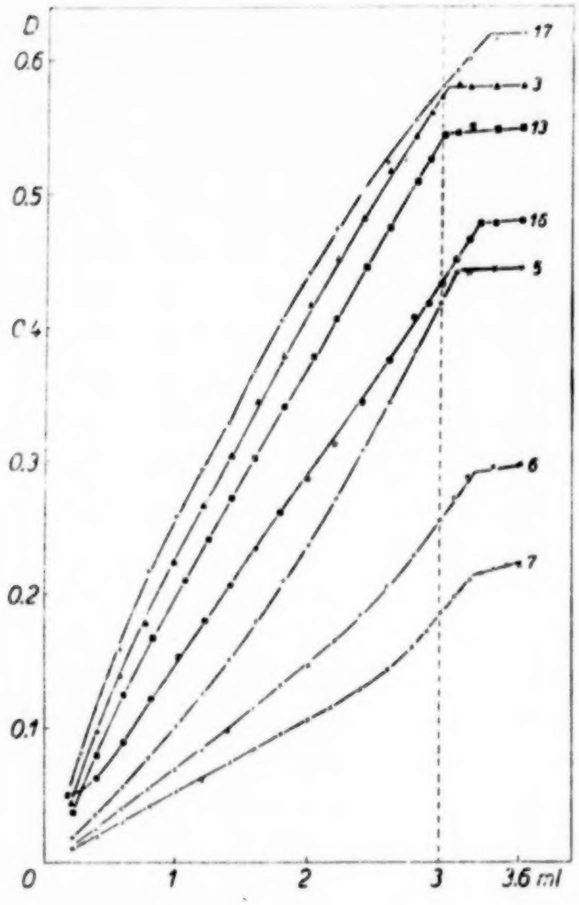

Fig. 1
Titration curves of sulfuric acid with barium nitrate

density values obtained were lower and the results were not definite. Thus working with the maximum amount of sulfuric acid (3 ml 0.02M) in aqueous solution no certain maximum density point was obtained and the density value was about one-third of the value which was obtained in the optimal alcoholic-water mixture. The influence of these mixtures on the velocity of chemical reactions has been discussed more extensively elsewhere[4]. Table I, Experiments 1-7 (and Fig. 1) show the influence of increasing amounts of ethyl alcohol on the heterometric results. Between 10% and 20% alcohol, no difference in the results could be detected in the absence of hydrochloric acid. On further increasing the amount of alcohol, the maximum optical density gradually decreased. At the same time the errors became greater and the end-point was displaced beyond that calculated. Experiments 9 and 10 show that the addition to the 20% alcoholic solution of hydrochloric acid in a somewhat larger amount, decreased the maximum optical density values and that the analytical end-points which were obtained too early, were uncertain. The results which are obtained in the presence of hydrochloric acid in 50% alcoholic solutions (expts. 11-15) are clearer and very interesting. If these results are compared with those of experiment 7, it can be seen that the addition of hydrochloric acid counteracted the deteriorating effect of larger amounts of alcohol. On increasing the acid concentration, optimal working conditions were soon obtained. Thus hydrochloric acid may be present in solution in high concentration (0.4N). Perchloric acid acts like hydrochloric acid (expt. 18).

Experiments 19-23 show results obtained with extremely low quantities of sulfuric acid. Even an 0.0015M sulfuric acid solution could still be titrated (expt. 22) in 50% alcoholic solution in the presence of 0.05N hydrochloric acid, and the error was normal.

b. *Influence of supplements*

Influence of acids. These experiments were all carried out in 50% alcoholic solution which also contained sufficient hydrochloric acid to give optimum working conditions. Tables I and II and Fig. 1 and 2 show some of the results obtained in the presence of mono- and polybasic acids. When *nitric acid* was used instead of hydrochloric acid (expts. 16 and 17) large errors were found. Although the maximum density values were as usual, the analytical end-points obtained were too late and excesses of barium nitrate were used for the titration. Probably, barium nitrate is coprecipi-

TABLE I

General composition: 3 ml H_2SO_4 aM + b ml alc. + (6-b) ml H_2O +
1 ml acid + x ml $Ba(NO_3)_2$ aM alc. Temp. = 20° C

Expt. No.	*Solutions*				*Found*			
	molarity (= a)	*% alcohol*	*acid*		*ml $Ba(NO_3)_2$ (= x)*	*Max. opt. density value*	*Approx. titration time (min)*	*% error*
			name	*normal*				
1	0.02	10	—	—	3.07	0.53	7	2.3
2	0.02	15	—	—	3.00	0.50	9	0.0
3	0.02	20	—	—	3.02	0.58	5	0.7
4	0.02	25	—	—	3.06	0.47	6	2.0
5	0.02	30	—	—	3.12	0.41	8	4.0
6	0.02	40	—	—	3.25	0.30	12	8.3
7	0.02	50	—	—	3.26	0.22	9	8.6
8	0.02	20	HCl	0.5	3.00	0.44	12	0.0
9	0.02	20	,,	1.0	2.87	0.40	9	−4.3
10	0.02	20	,,	2.0	2.5	0.29	27	10.0
11	0.02	50	,,	0.5	3.16	0.35	9	5.3
12	0.02	50	,,	1.0	3.04	0.46	7	1.3
13	0.02	50	,,	2.0	3.02	0.55	5	0.7
14	0.02	50	,,	3.0	3.10	0.53	12	3.3
15	0.02	50	,,	4.0	3.03	0.57	12	1.0
16	0.02	50	HNO_3	1.0	3.3	0.48	5	10.0
17	0.02	50	,,	2.0	3.34	0.60	15	11.3
18	0.02	50	$HClO_4$	2.0	3.10	0.60	9	3.3
19	0.005	20	—	—	2.95	0.19	13	−1.6
20	0.005	20	HCl	0.5	2.9	0.14	20	−3.3
21	0.005	50	—	—		0.05	13	
22	0.005	50	HCl	0.5	2.94	0.19	13	−2.0
23	0.005	50	,,	2.0	2.78	0.21	26	7.3

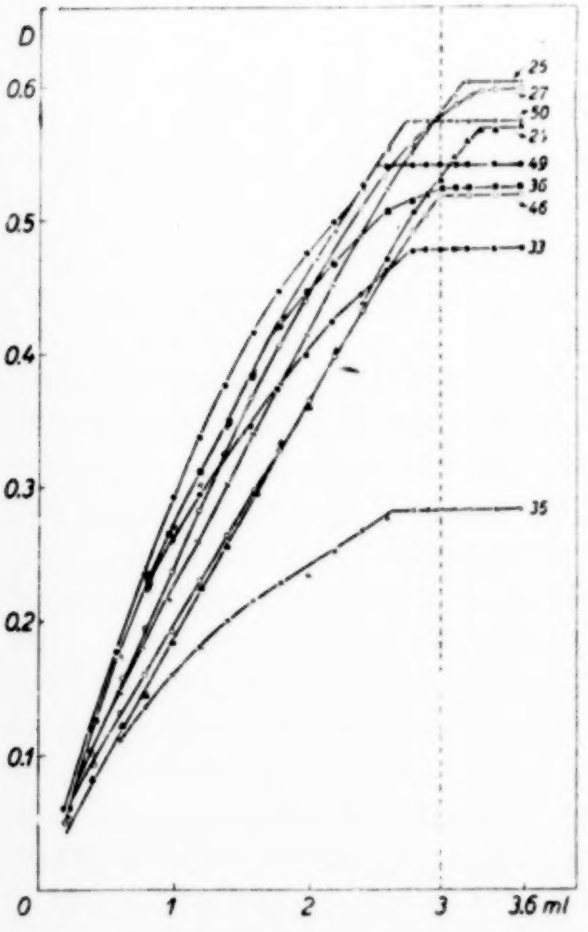

Fig. 2. Titration curves of sulfuric acid with barium nitrate.

tated together with the barium sulfate. Apparently, this phenomenon does not interfere with the character of the particles which absorb the light. No improvement was observed when nitric acid was added *in addition* to the optimal amount of hydrochloric acid (Table II, exp. 27). In contrast to this, perchloric acid had no influence (expt. 28). Neither a 0.1M *acetic*, nor a 0.1M *citric* acid (expts. 29 and 30) had any influence on the results. In contrast to this, *phosphoric* acid had a deleterious effect in a similar direction to nitric acid: more barium nitrate had to be used for the titration although the maximum density value remained as high as usual. If a 0.1N phosphoric acid was used instead, there was no deteriorating effect, and normal results (expt. 26) were obtained.

Influence of polyvalent cations. The results obtained with trivalent cations were

TABLE II

General composition: 3 ml H_2SO_4 0.02*M* + 1 ml HCl 2*N* + 1 ml supplements + 5 ml alc + *x* ml $Ba(NO_3)_2$ 0.02*M*, 50% alc. Temp. = 20° C

Expt. No.	*Supplement*	*Found*				*Remarks*
		ml $Ba(NO_3)_2$ (= x)	*Maxim. opt. density value*	*Approx. titration time (min)*	*% error*	
24	H_3PO_4 *M*	3.30	0.57	17	+10.0	
25	,, 0.66*M*	3.15	0.60	9	+5.0	
26	,, 0.33*M*	3.06	0.52	11	+2.0	
27	HNO_3*M*	3.3*	0.60	13	+10.0	
28	$HClO_4$	2.98	0.61	11	−0.7	
29	Acetic ac. *M*	3.07	0.56	5	+2.3	
30	Citric ac. *M*	3.05	0.56	6	+1.7	
31	$AlCl_3$ *M*	3.0	0.54	12	0.0	
32	$CrCl_3$ *M*	?	0.30	15		
33	,, 0.5*M*	2.76*	0.48	16	−8.0	
34	,, 0.2 ,,					big flakes
35	$FeCl_3$ 0.5*M*	2.64*	0.28	30	−12.0	with red filter
36	,, 0.2 ,,	3.00	0.52	14	0.0	
37	0.5 ml $FeCl_3$ 0.5*M* + 0.5 ,, Citric ac. 2*M*	2.6?				agglomeration
38	0.5 ml $FeCl_3$*M* 0.5*M* + 0.5 ,, H_3PO_4 *M*	2.8*	0.46	12	−6.6	
39	$MgCl_2$ 2*M*	2.96	0.53	20	−1.3	
40	$ZnCl_2$ *M*	3.04	0.53	17	0.0	
41	$CoCl_2$ *M*	3.06	0.59	13	+2.0	
42	$Co(NO_3)_2$ *M*	3.16	0.51	21	+5.3	
43	$Ni(NO_3)_2$ *M*	3.07	0.63	7	+2.3	
44	$MnCl_2$ *M*	3.00	0.52	10	0.0	
45	$Cd(NO_3)_2$ *M*	3.04	0.55	18	+1.3	
46	$CuCl_2$ *M*	3.00	0.52	20	0.0	
47	NaCl 2*M*	2.92	0.60	9	−2.7	
48	NH_4Cl 2*M*	2.97	0.54	15	−1.0	
49	KCl 2*M*	2.52	0.54	11	−16	
50	,, *M*	2.75	0.58	9	−8.3	
51	,, 0.5*M*	2.90	0.57	14	−3.3	
52	,, 0.2*M*	2.95	0.59	12	−1.7	

different. A 0.1*M* *aluminium chloride* (expt. 31) had no influence whatever whilst iron and chromium chloride both interfered. *Chromium chloride* lowered to some degree the maximum density values (expts. 32 and 33) and less barium nitrate was then necessary for the titration. In addition, the location of the end-point was unsure. If present in lower concentration (expt. 34) flakes were formed and the titration became impossible. *Iron chloride* when present in a concentration of 0.05*M* (expt. 35) $[Fe^{+3}]$: $[SO_4^{-2}]$ = 9 : 1) depressed the maximum density value very considerably and *less* barium nitrate than calculated was used for the titration. Both chromium and iron apparently consume the sulfate anion which was coprecipitated as salt together with barium sulfate and therefore less sulfate was available for the titration. It is very interesting that iron chloride which was present in 0.02*M* concentration ($[Fe^{+3}]$: $[SO_4^{-2}]$ = 3 : 1) no longer influenced the normal titration (expt. 36). Neither the presence of citric nor phosphoric acids (expts. 37 and 38) improved the results in mixtures of these acids with iron. In the latter case the iron and the phosphate ions acted in opposite directions and as a result somewhat less barium nitrate than calculated was used for the titration, thus indicating that the effect of iron prevails. Therefore, it may well be that if the concentration of both ions were properly balanced, no disturbance would occur. An attempt was made to titrate the iron using a red filter but improved results could not be achieved, (expt. 33).

Influence of bivalent cations. As Table II shows, the different bivalent cations, almost without exception, had no influence on the results, if they were present in solution in a 0.1 *M* concentration ($[Me] : [SO_4^{-2}] = 16.6 : 1$). It is interesting to note that the cadmium and the nickel (expts. 43 and 45) were present as *nitrates*, but nevertheless the influence of the anion was not perceptible. Only in the presence of cobalt did interference occur (expt. 42), but this interference probably differs from that of other interfering cations because more barium nitrate was used for the titration instead of less, as usual.

Influence of monovalent cations. Only the alkali metals were tested. *Sodium* and *ammonium* chlorides (expts. 47 and 48) in 0.2*M* concentration had no influence on the results. In contrast to these was the behaviour of *potassium* chloride (expts. 49 and 50). Here too, as with iron, a distinction must be drawn between the influences caused when potassium chloride was present in lower and in higher concentrations. In the latter case, less barium was used at the end-point for the titration, although the maximum density value did not change (in contrast to iron!). When the potassium chloride was present in lower concentrations (expt. 52) ($= 0.02M$) ($[K^+] : [SO_4^{-2}] = 3 : 1$) it did not interfere any more.

DISCUSSION

If the results which are obtained in the presence of disturbing cations or anions are summarized, it can be seen that interference occurs only when the ions are present in a molar concentration *many* times greater than that of the sulfate anion. This interference is no longer perceptible at the molar ratio of $[ion] : [SO_4^{-2}] = 3 : 1$ and it can therefore be assumed that the interference is not caused by adsorption but that coprecipitation occurs. This is clearly shown in the following cases: phosphoric acid consumed barium ions being coprecipitated as barium phosphate, and therefore *more* barium was used than calculated for the titration. Potassium ions consume sulfate anions being coprecipitated as potassium sulfate and therefore *less* barium was used. In contrast to this the ammonium cation did not interfere because of the high solubility of ammonium sulfate. The nitrate anion is coprecipitated as barium nitrate and *more* barium was used for the titration. As the ferric ion did not interfere at somewhat lower concentrations, it must be assumed that in this case also, interference by coprecipitation as iron sulfate (anhydrous?) occurred. The problem as to why the bivalent cations did not interfere by coprecipitation still remains to be clarified.

The influence of alcohol-water mixtures and the opposing effect of hydrochloric acid and ethyl alcohol in such mixtures, is more complicated[4-5]. Some time ago the effect of alcohol water mixtures on the velocity of chemical reactions, was studied by one of us (M.B.)[4]. This would be a parallel case to the precipitation of barium sulfate and the effect of alcohol on the particle size. It was then found that alcoholic-water mixtures which contain less than $\sim$ 25% alcohol still act as pure water solutions. In contrast to this, a 50% alcoholic solution acts as a *mixture* of alcohol and water. The effect of hydrochloric acid may therefore be explained as binding the free alcohol molecules and thus cancelling the deteriorating effect of excess of ethyl alcohol. Working in 50% alcoholic solution, which contains hydrochloric acid, the heterometric titrations can be carried out successfully in the presence of high concentrations of strong acid.

Analytical aspects

Apart from a few exceptional cases, sulfuric acid can easily be titrated with barium nitrate in strong hydrochloric acid 50% alcoholic solution. A titration takes about 10 minutes, at room temperature, and the error is 0-3%. 10 ml of a sulfate solution containing 1.5-6 mg sulfuric acid is necessary for a titration.

The presence of phosphate, nitrate, ferric, chromium(III) or potassium ions interferes with the results, but if they are present in a molar ratio of ≤ 3 to 1 $[SO_4^{-2}]$ no interference occurs.

Analysis

Technique. Barium nitrate is added drop by drop from a 5 ml microburet (0.01 ml) and the solution is stirred vigorously. The precipitation begins immediately and the readings on the galvanometer are taken only when they become constant, which generally takes a few seconds to a minute. An enlarged titration curve is drawn which has as abscissa the density values measured, and as ordinate the volume of barium nitrate added. The end-point is obtained by the intersection of the line of the last part (the last quarter) of the titration curve with the horizontal maximum density line.

Method. 5 ml aqueous solution containing a few mg sulfuric acid (or sulfate) and 1 ml 2*N* hydrochloric acid is mixed with 5 ml alcohol. The solution is titrated heterometrically with a 50% alcoholic solution of 0.01-0.02*M* barium nitrate. Titration time is 10 minutes. Error 0-3%.

SUMMARY

The influence of the medium on the precipitation of barium sulfate both in the presence and in the absence of various concentrations of acids, was studied.

The coprecipitation, which occurs in the presence of varying concentrations of phosphoric and nitric acids, as well as in the presence of iron(III), chromium or potassium ions, was studied quantitatively.

A quick method is presented for the micro-determination of sulfuric acid.

RÉSUMÉ

L'influence du milieu sur la précipitation de $BaSO_4$ a été étudiée, en l'absence et en présence de diverses concentrations d'acides. La coprécipitation, qui apparaît en présence de différentes concentrations d'acides phosphorique et nitrique, ainsi qu'en présence des ions du fer(III), du chrome et du potassium, a été étudiée quantitativement. Une méthode rapide est proposée pour le microdosage de l'acide sulfurique.

ZUSAMMENFASSUNG

Der Einfluss des Milieus auf die Abscheidung von Bariumsulfat in An- sowie Abwesenheit von Säuren verschiedener Konzentrationen wurde studiert.

Die Kopräzipitation, welche in Anwesenheit von verschieden konzentrierter Phosphor- und Salpetersäure sowie von Eisen(III), Chrom- und Kalium-Ionen stattfindet, wurde quantitativ verfolgt.

Eine rasche Methode für die Mikro-Bestimmung von Schwefelsäure wurde vorgeschlagen.

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THE FLOWING MERCURY ELECTRODE IN POLAROGRAPHY. PART I

by

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Polarographic studies in hydrofluoric acid media were first reported by CLIFFORD AND BALOG[1] in 1951. These investigators prepared a dropping mercury electrode from a rod of polytrifluorochlorethylene by drilling, softening and drawing down to size on a 0.03 mm tungsten wire mandrel. Considerable difficulty was experienced in carrying out this process and the resulting capillary failed to give a consistently reproducible drop time, tending to produce a spray rather than discrete mercury drops. An alternative electrode was prepared consisting of a platinum tube of small bore embedded in a sheath of polytrifluorochlorethylene. This electrode also failed to yield a consistently reproducible drop time and furthermore possessed some of the undesirable features of noble metal electrodes. Nevertheless, the practicability of using rotating micro-electrodes of platinum and nickel in hydrofluoric acid media was subsequently explored by SARGENT, CLIFFORD AND LEMMON[2] in 1953 with some measure of success. However the polarographic phenomena associated with solid microelectrodes have yet to be subjected to a satisfactory mathematical interpretation; a new approach to the problem of electrode design for hydrofluoric acid media was therefore attempted by the authors.

A small number of dropping electrode capillaries were prepared by drawing down in a flame standard polyethylene tubing of of 12 mm bore, 6 mm wall. This technique yielded a number of serviceable electrodes giving reproducible drop times initially, but after a period of use these electrodes tended to develop drop times which were both extended and erratic. Capillaries having walls of varying lengths and thickness were prepared and tested, but the tendency for lengthening of the drop time appeared to be independent of the dimensions of the capillary wall. The persistence of the erratic behaviour led to the abandonment of further development work on polyethylene dropping mercury electrodes, and attention was focussed on the Heyrovsky streaming mercury electrode[3] as a possible alternative. The design of this electrode was particularly attractive for hydrofluoric acid polarography since the mercury nozzle could be readily fabricated in polyethylene or polytrifluorochlorethylene. However, the stirring of the solution caused by the passage of the jet of mercury, together with the heavy mercury consumption, were factors which could not be ignored in assessing the potentialities of the streaming mercury electrode.

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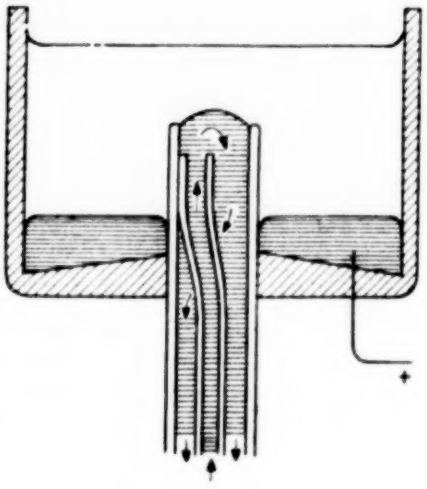

Fig. 1. Polarographic cell with flowing mercury cathode.

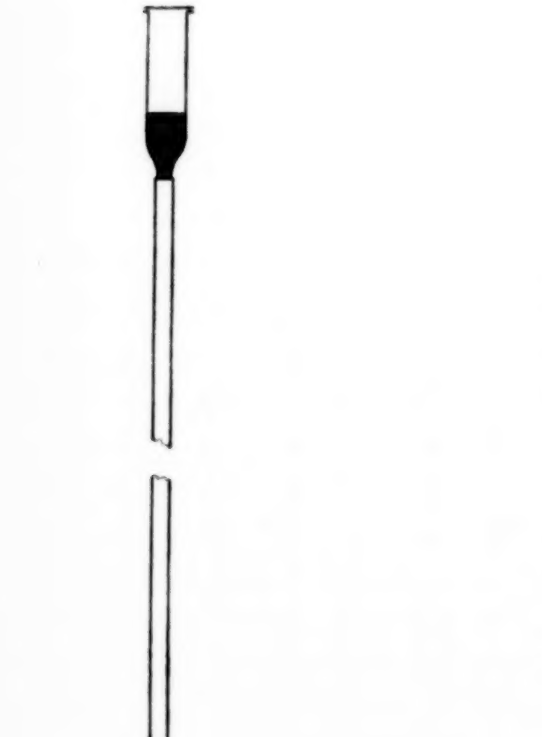

Fig. 2. General arrangement of polarographic cell, amalgam reservoir and dropping mercury electrode assembly.

Consideration was also given to other types of electrodes; but no design yet published was found to be entirely suitable for accurate fundamental polarographic studies in hydrofluoric acid media. Simonnin and Quintin[4] had employed a mercury column renewed by a succession of mercury drops falling from a capillary; Leveque[5] had allowed mercury to flow down the surface of an amalgamated platinum wire; Cooke[6] used an amalgamated silver wire which was rotated at high speed; Lee[7] had devised a rotating mercury electrode, while Streuli and Cooke[8] had studied the characteristics of the stationary mercury pool electrode. The design of the latter electrode seemed particularly suitable at first but unfortunately the diffusion layer tended to increase in thickness with time and, of course, the surface of the mercury pool was not renewed.

It was therefore decided that an attempt should be made to design a new electrode suitable for use in hydrofluoric acid media and combining the advantages of the streaming and dropping mercury electrodes. It was felt that such an electrode should possess a constant surface area but with a renewable surface; the mercury consumption should be economical and the movement at the mercury-electrolyte interface should be as small as possible. Simplicity of design was essential in order that the electrode could readily be fabricated in polyethylene or polytrifluorochlorethylene. To simplify the mathematical interpretation of the polarographic waves it was considered desirable that the reducible ionic species should reach the electrode by diffusion only, unassisted by stirring or convection currents. The requirement of a renewable surface restricted the choice of electronic conductor to mercury or amalgam; mercury was selected for the initial design. A constant surface area could be assured by containing the mercury within an open vertical tube of uniform bore; in order that the surface layer of the mercury should be renewed with the minimum disturbance the fresh mercury would be supplied from a source located within the mercury column. These considerations led to the development of the electrode in Fig. 1, known as the flowing mercury electrode[9].

DESCRIPTION OF ELECTRODE

A column of mercury is contained within a vertical polyethylene tube of 2 mm bore, 0.5 mm wall thickness. The surface layer of the column is continuously renewed by means of a stream of pure mercury issuing from an internal supply tube of 0.5 mm bore, 0.25 mm wall thickness. Control of the fresh mercury supply is exercised by means of an orthodox glass dropping mercury electrode assembly (Fig. 2) from which mercury flows at the desired rate into a funnel connected to the internal supply tube (Fig. 3). A pressure head in the funnel of approximately 10 mm Hg is sufficient to produce the required rate of flow of mercury through the internal supply tube to the electrode surface. The displaced amalgam passes through the annular space surrounding the internal supply tube and finally returns to a reservoir of large surface area. The potential of the polarizable electrode is applied by means of a platinum wire in contact with the amalgam in the reservoir.

The non-polarisable electrode consists of a mercury pool in the base of a polyethylene cell surrounding the polarizable electrode. The pool potential is applied by means of a platinum wire inserted through the cell base. An alternative cell has also been designed which permits the use of standard reference electrodes.

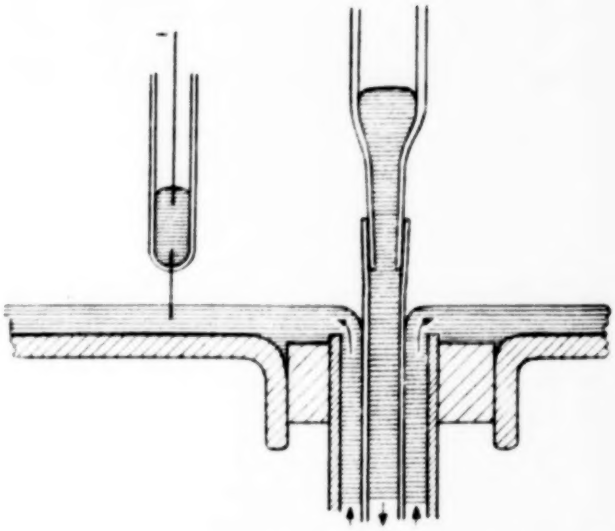

Fig. 3. Arrangement of the mercury supply tube within the electrode tube at the junction with the amalgam reservoir.

The polarizable electrode functions most effectively when the periphery of the mercury meniscus is close to or level with the top of the electrode tube; the diffusion currents are then invariant with time, thus conforming with the condition for spherical diffusion. On the other hand if the meniscus is withdrawn to a depth of 2 cm or more below the rim of the electrode tube, it is found that the diffusion currents decrease with time in a hyperbolic manner suggesting that under these conditions the diffusion may be linear in character (Fig. 4).

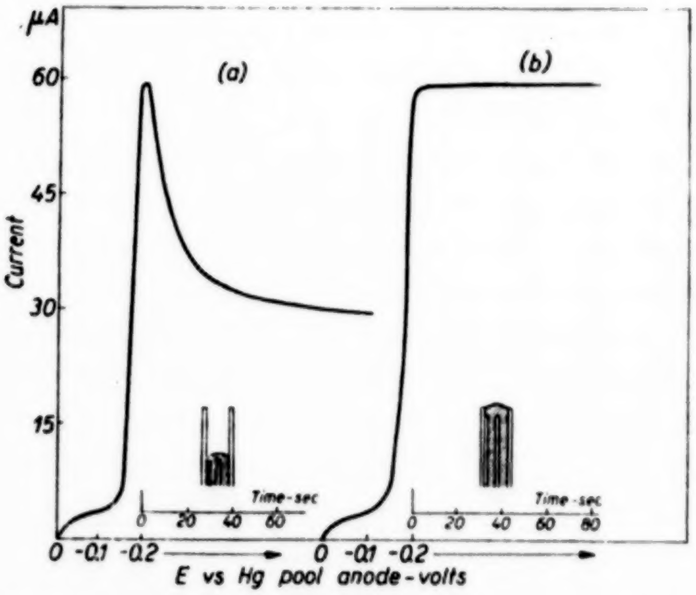

Fig. 4. Influence of meniscus position on the diffusion current for 2.05 m*M* Sb^{+3} in normal hydrochloric acid.
(a) Shielded meniscus. — Linear diffusion curve.
(b) Exposed meniscus. — Spherical diffusion plateau.

The height of the column of mercury in the electrode tube is governed partly by the level of the amalgam in the reservoir and partly by the rate of supply of fresh mercury. The rate of supply of fresh mercury is equal to the rate at which mercury issues from the dropping mercury electrode; this rate is reasonably constant and normally produces a kinetic head at the electrode of $1^1/_2$ mm Hg. Thus mercury height control may be exercised solely by adjustment of the height of the reservoir. In practice accurate control is more conveniently obtained by adjustment of the height of the electrode and cell with respect to the reservoir by means of a micrometer screw attached to the cell mounting. The reservoir has a surface area of 236 sq.cm, and affords adequate capacity for amalgam thus effectively preventing any significant change in meniscus level at the electrode. The cell has a remarkably low resistance of the order of tens of ohms.

The top of the feed tube is normally positioned $1^1/_2$ mm below the crown of the meniscus; if the feed tube is withdrawn below this level the diffusion currents develop pronounced maxima. These maxima progressively disappear when the feed tube is gradually restored to its normal position (Fig. 5).

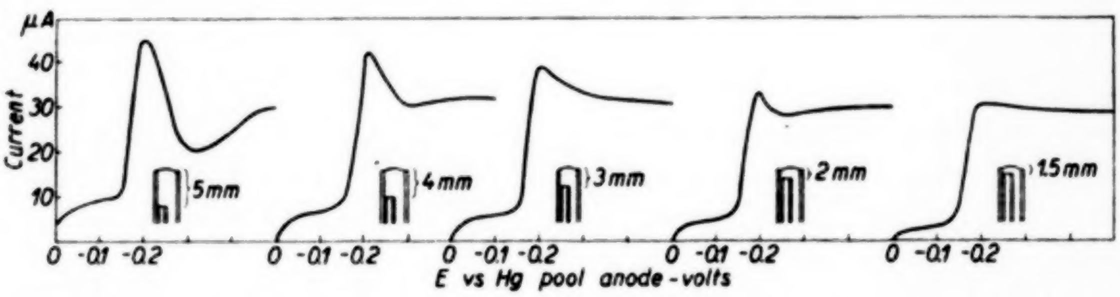

Fig. 5. Influence of position of feed tube on the diffusion current for 2.05 m*M* Sb^{+3} in normal hydrochloric acid. Diffusion current curves produced with Hg feed tube at varying depth below meniscus.

RESULTS

The polarographic waves obtained with air-free solutions of antimony trioxide in normal hydrochloric acid are found to be reproducible (Fig. 6). The waves are similarly shaped to those obtained with the dropping mercury electrode. Furthermore the continuous character of the mercury feed permits the waves to be recorded as smooth curves without the oscillations which characterise the waves obtained at the dropping mercury electrode. Oxygen interferes and must be removed from the solution by passing oxygen-free nitrogen for 15 minutes.

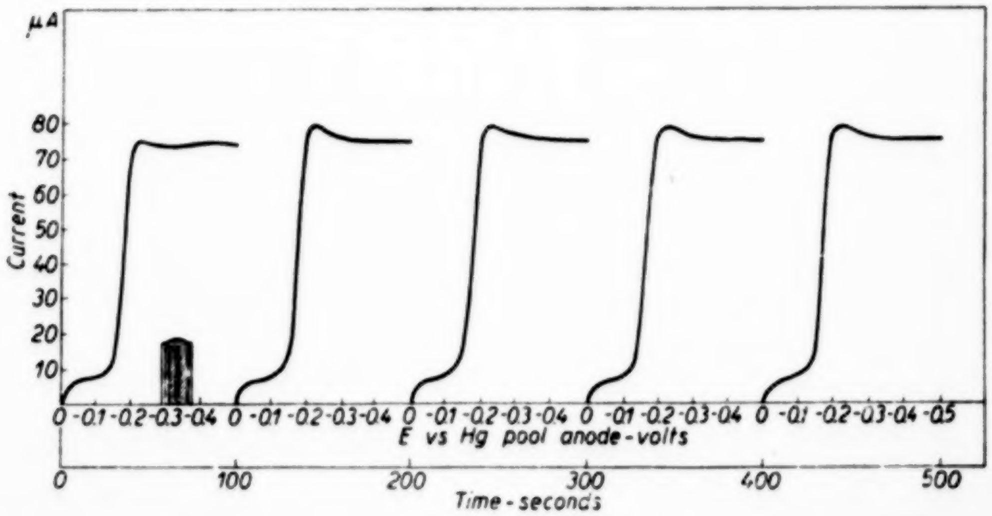

Fig. 6. Reproducibility of diffusion current. Polarograms for 2.2 m*M* Sb^{+3} in normal hydrochloric acid.

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Polarographic waves for solutions of varying antimony concentration[9] are shown in Fig. 7. A plot of the wave height against concentration shows a linear relationship (Fig. 8) indicating that diffusion currents are proportional to the concentration of the trivalent antimony ion. The log plot of the wave yields a straight line having a reciprocal slope of 0.020 volts, the theoretical value for a 3-electron reduction, indicating that at a flowing mercury electrode trivalent antimony is reversibly reduced (Fig. 9). The half wave potential of —0.16 volts measured against the mercury pool anode agrees with the values obtained by other workers for the reduction of trivalent antimony in normal hydrochloric acid using the dropping mercury electrode[10-18].

It might be expected that electro-capillarity at the flowing mercury electrode would manifest itself by a vertical displacement of the mercury meniscus during the application of a varying potential. This aspect has accordingly been investigated with the aid of a travelling microscope, over the applied negative potential range 0 - 2.6 volts against the mercury pool anode with solutions of lead nitrate of 1 m*M* and 0.5 m*M* strength. Comparative tests were also carried out with no flow of mercury at the electrode. In each case ten tests were carried out over the full voltage range, five tests being run with increasing negative potential and five with decreasing potential. The variation between tests of a similar kind was found to be insignificant; the results have been averaged and the mean values are shown plotted against potential in Fig 10. At potentials below 0.2 volts

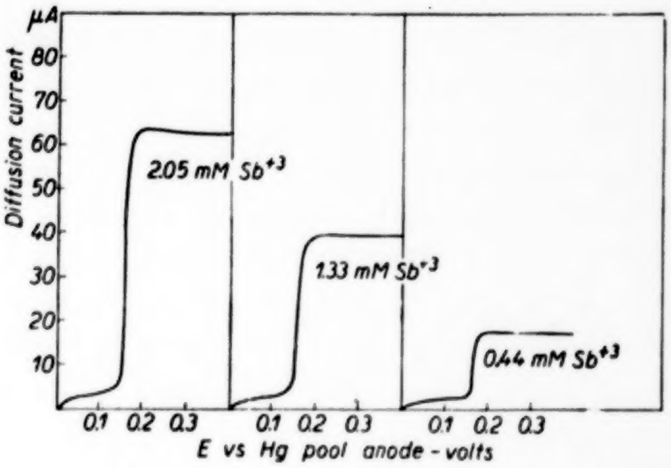

Fig. 7. Influence of concentration of reducible ion on the diffusion current for solutions of Sb_2O_3 in normal hydrochloric acid.

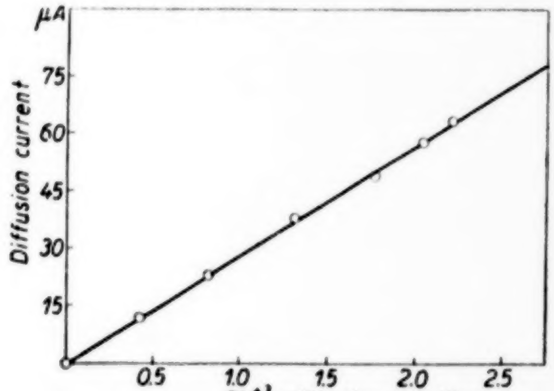

Fig. 8. Concentration-Diffusion current relation ship for the polarographic waves shown in Fig. 7.

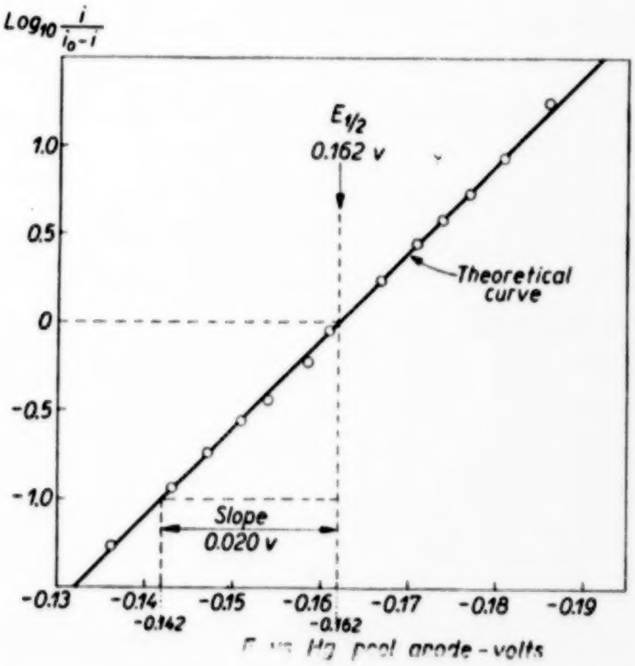

Fig. 9. Plot of log $\frac{i}{i_d - i}$ for the reversible reduction of Sb^{+3} in normal hydrochloric acid at the the flowing mercury electrode.

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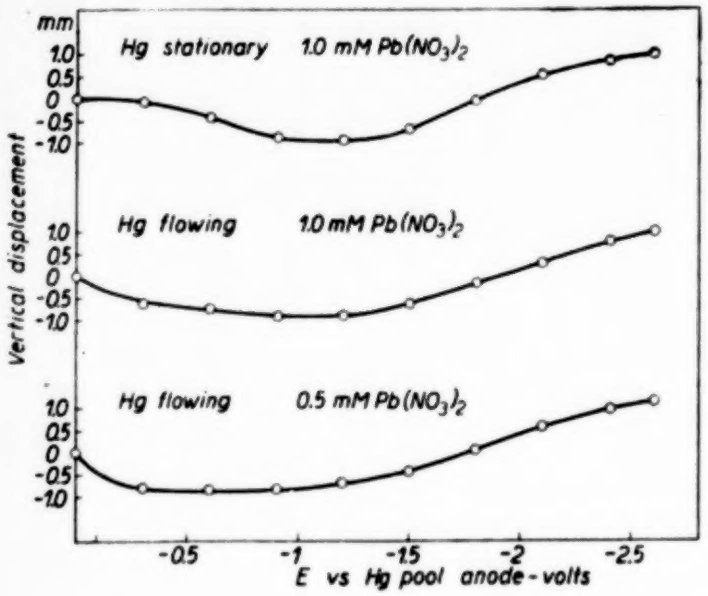

Fig. 10. Influence of electro-capillarity at the flowing mercury electrode.

the displacement of the meniscus is insignificant but at potentials approaching 0.5 volts the vertical displacement approaches 1 mm in magnitude. It will be noted that the shape of the curves reflects the electro-capillary curve for mercury.

The effect of repeated polarographic reduction at a stationary mercury surface has also been investigated. The resulting current-voltage curves are shown in Fig. 11. As would be expected these curves have a similar shape to the curve obtained with mercury flowing but with the feed tube withdrawn to a depth of 5 mm below the electrode surface (Fig. 6). It is significant that, after a series of five runs with a static mercury surface, the current maximum increased in magnitude by over 20% but that a change of surface produced a restoration of the maximum current to the initial value once more.

The polarograms recorded in this paper were obtained with a Cambridge Photographic Recording Polarograph. Polarographic studies in fluoride media with the flowing mercury electrode are proceeding and will be reported in Part II.

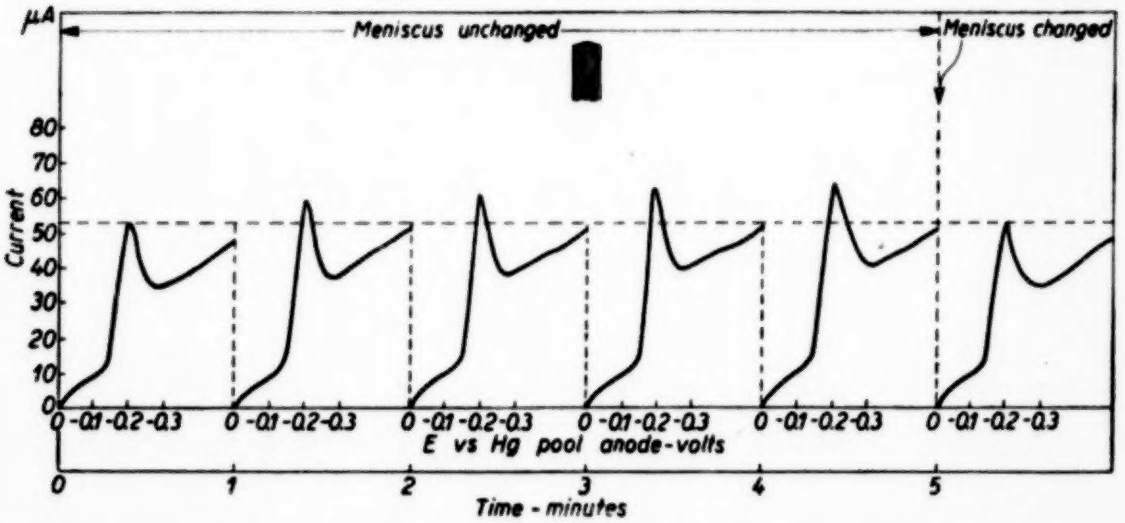

Fig. 11. Polarographic waves obtained with a stationary mercury surface exposed at the electrode tube. — Curves obtained with fresh, stagnating and renewed mercury surfaces.

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SUMMARY

A polarisable electrode of constant surface area is described in which the surface layer of a column of mercury is continuously renewed from an internal mercury supply. Reproducible diffusion currents are obtainable which do not exhibit maxima. Wave heights are proportional to the concentration of reducible ion. The mercury consumption is similar to that of the dropping mercury electrode. The electrode and cell are constructed throughout in polyethylene.

RÉSUMÉ

Une électrode polarisable est décrite, où la surface de mercure de la colonne est continuellement renouvelée. Des courants de diffusion reproductibles peuvent être obtenus, ne présentant pas de maxima. Les hauteurs des sauts sont proportionnelles à la concentration de l'ion réduit. La consommation de mercure est la même que celle de l'électrode à gouttes de mercure. L'électrode et la cuve sont entièrement faites en polyéthylène.

ZUSAMMENFASSUNG

Es wird eine polarisierbare Elektrode beschrieben, wo die Oberfläche des Quecksilbers ständig erneuert wird. Es können reproduzierbare Diffusionsströme erhalten werden, welche keine Maxima aufweisen. Die Höhen der Sprünge sind proportional der Konzentration des reduzierten Ions. Der Verbrauch an Quecksilber ist der gleiche wie der, der Tropfelektrode. Die Elektrode und die Zelle sind ganz aus Polyäthylen hergestellt.

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ÉTUDE DE LA PHÉNYL-2 OXINE ET DE SES CHÉLATES
III. PRÉPARATION ET PROPRIÉTÉS DES PHÉNYL-2 OXINATES

par

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Dans deux précédents articles de cette Revue[1,2], nous avons indiqué les principales caractéristiques de la phényl-2 oxine (phényl-2 hydroxy-8 quinoléine). Mais une propriété essentielle de cette phényl-2 oxine, comme de l'oxine dont elle dérive, est de pouvoir former avec les ions métalliques des "complexes internes de chélation" (plus brièvement, des "chélates"), dans lesquels la coordinence de l'ion central est souvent complétée par l'addition de molécules d'eau (par exemple).

On sait que dans la formation de tels composés, il faut fréquemment faire intervenir la notion d'empêchement stérique. En particulier, pour les dérivés α-substitués de l'oxine, certains chélates sont exclus, les autres voient leur stabilité modifiée ainsi que le nombre de leurs molécules d'eau de cristallisation.

D'où l'intérêt d'une étude des phényl-2 oxinates qui permette la comparaison des résultats avec ceux précédemment publiés pour les oxinates[3,4] et les méthyl-2 oxinates[3,5].

I. ÉTUDE POTENTIOMÉTRIQUE DE LA PRÉCIPITATION

Une telle étude permet d'atteindre les produits de solubilité ou les constantes de stabilité des chélates. Mais pour effectuer une comparaison valable des différents réactifs, il eut fallu pouvoir les étudier dans les mêmes conditions. Or, nous savons[1] que la phényl-2 oxine est beaucoup moins soluble dans l'eau que l'oxine ou la méthyl-2 oxine, et qu'il est nécessaire d'opérer, par exemple, en milieu hydro-alcoolique; il en résulte évidemment un certain décalage des valeurs observées par rapport au milieu aqueux.

Nous avons cependant établi[6] des courbes de neutralisation, qui nous ont au moins permis de situer les zônes de formation des chélates.

Ces courbes, dont trois exemplaires sont reproduits sur la Fig. 1, ont été obtenues dans les mêmes conditions (milieu hydroalcoolique 45° G.L.) que la courbe de neutralisation de la phényl-2 oxine précédemment décrite[2]: on ajoutait simplement au milieu la quantité théorique d'ions métalliques.

Sur ces courbes, la formation de chélate se traduit par l'apparition d'un "palier", que nous repérons par le point d'inflexion M. On notera, tout particulièrement dans le cas du phényloxinate de zinc (courbe 1), qu'il faut faire la distinction entre la

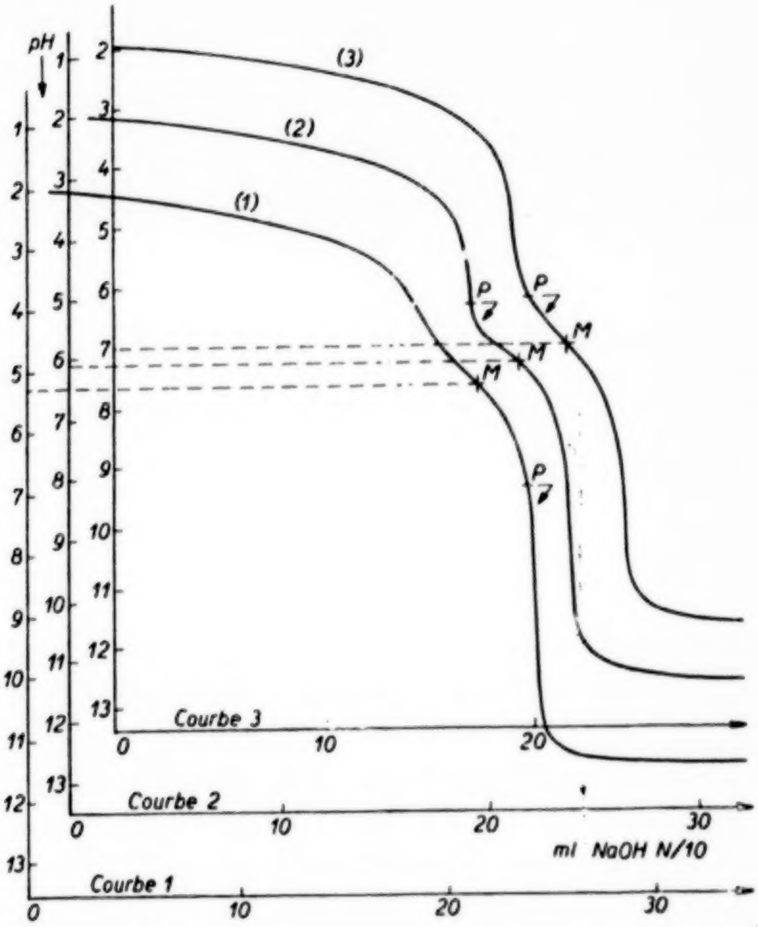

Fig. 1. Potentiométrie des phényloxinates.
Courbe 1: Zn; courbe 2: Cd: courbe 3: Ni.

formation d'un chélate et sa précipitation. Nous donnons dans le Tableau I, pour une série de cations bivalents, les pH de début de précipitation (points P) et les ,,pH de formation'' (points M).

TABLEAU I

Cation	*pH de début de précipitation*	*pH de formation*
Zn^{+2}	6.90	5.30
Cd^{+2}	5.20	6.15
Ni^{+2}	6.30	7.05
Co^{+2}	6.30	6.95
Hg^{+2}	6.45	7.30
Mn^{+2}	7.55	8.30
Pb^{+2}	4.05	6.00
Cu^{+2}	2.75	<4

Des courbes plus complexes ont été obtenues[6] avec Fe^{+2}, Fe^{+3}, Tl^{+3}, MoO$_4^{-2}$, WO$_4^{-2}$, VO$_3^{-}$. Parmi les précipités correspondants, seuls ceux de Tl, Mo et Fe^{II} se sont révélés à l'analyse thermogravimétrique être des produits définis.

Enfin, ni Al^{+3}, ni Mg^{+2}, ni Cr^{+3} ne donnent lieu à la formation d'un chélate, alors que l'on connaît les méthyl-2 oxinates de Mg et Cr et les oxinates de Al, Mg et Cr. Un certain accroissement de sélectivité a donc bien été obtenu par l'introduction du groupement phényle à la place du groupement méthyle, en α de l'atome d'azote de l'oxine.

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II. ANALYSE THERMOGRAVIMÉTRIQUE DES PHÉNYL-2 OXINATES

Préparation des phényl-2 oxinates

Le mode opératoire utilisé par Borrel et Pâris[4,5] pour les oxinates et méthyl-2 oxinates ne s'applique pas à la phényl-2 oxine: il faut en effet opérer en milieu hydroalcoolique. Or, il arrive que si l'on ajoute assez d'alcool (45 à 50%) pour empêcher toute coprécipitation du réactif, il n'est, dans certains cas (Zn, Co), plus possible d'obtenir la précipitation du chélate. Et, d'autre part, de telles teneurs en alcool gênent la fixation des molécules d'eau sur les chélates; on ne peut pas rassembler le précipité à chaud, sous peine de le déshydrater plus ou moins, voire même le dissoudre selon la quantité d'alcool présente.

A la suite de divers essais, nous avons adopté le mode opératoire suivant:

A des volumes égaux de la solution hydroalcoolique (45%) acide (*N*/5) du réactif (*M*/20) et de la solution aqueuse de l'ion métallique (*M*/40 pour un cation bivalent), on ajoute les quantités d'alcool et d'éther nécessaires pour que la proportion finale soit de 30% en alcool et 15% en éther. On provoque la précipitation en neutralisant progressivement, et sous agitation, par la soude normale. Le précipité est lavé deux fois par décantation avec un mélange eau-alcool 30% — éther 15%, recueilli sur creuset filtrant Pyrex no. 3 ou 4, et enfin, séché une nuit par aspiration d'un courant d'air à travers le filtre.

Nous avons cherché à obtenir des chélates possédant leur nombre maximum de molécules d'eau. Mais il n'est pas exclu qu'un autre mode opératoire puisse donner des résultats différents, comme nous avons pu l'observer pour l'oxinate de plomb (voir plus loin, Tableau III).

Analyse thermogravimétrique: mode opératoire

L'appareil utilisé était la thermobalance de Chevenard, avec, bien entendu, le même régime thermique que celui adopté par Borrel et Pâris pour leur étude des oxinates[4] et des méthyl-2 oxinates[5]: montée linéaire d'environ 3 degrés par minute jusqu'à 700° C et maintien 2 heures à cette température. On ne doit pas, en effet, perdre de vue, pour l'interprétation des résultats d'analyses thermogravimétriques de sources diverses, que ceux-ci dépendent non seulement du mode opératoire suivi pour la préparation du produit étudié, mais aussi du régime thermique utilisé.

La sensibilité de l'appareil était telle que 200 mg correspondaient à 154-155 mm sur le papier photographique.

Le poids initial de précipité analysé était de 300 à 400 mg. La perte de poids totale était connue en pesant le creuset avant et après l'opération; les pertes partielles étaient mesurées sur les courbes.

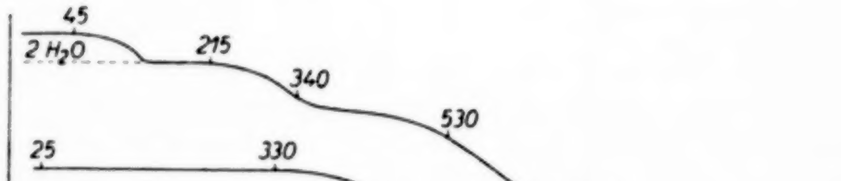

Fig. 2. Thermogravimétrie des phényloxinates.
Courbe 1: Cu; courbe 2: Zn; courbe 3: Cd.

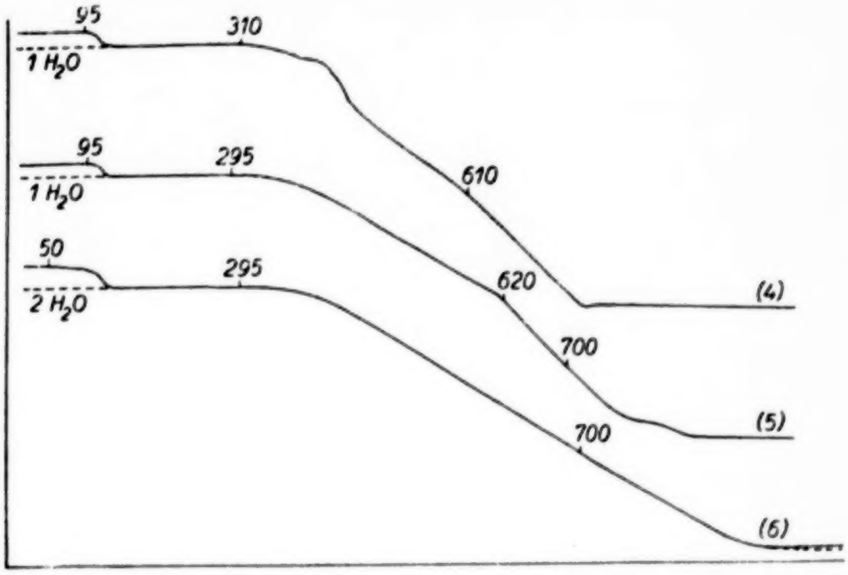

Fig. 3. Thermogravimétrie des phényloxinates.
Courbe 4: Ni; courbe 5: Co; courbe 6: Pb.

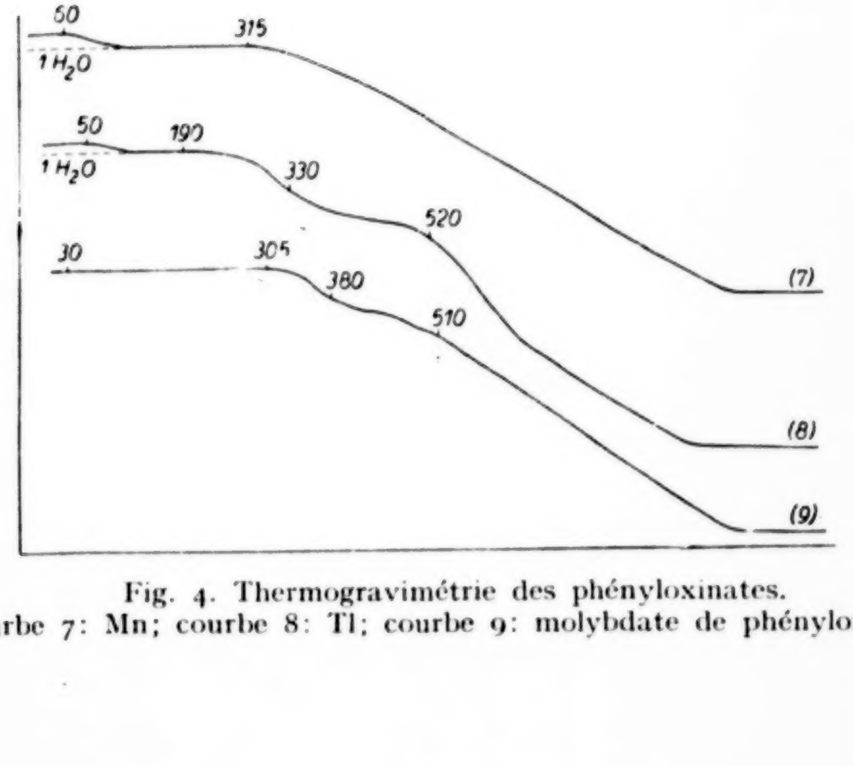

Fig. 4. Thermogravimétrie des phényloxinates.
Courbe 7: Mn; courbe 8: Tl; courbe 9: molybdate de phényloxine.

Résultats

Les courbes thermogravimétriques obtenues avec 9 chélates de la phényl-2 oxine sont reproduites dans les Figs. 2, 3 et 4. La présence ou non de molécules d'eau d'hydratation, les domaines de stabilité des chélates hydratés ou anhydres se déduisent facilement de ces courbes.

Le Tableau II rassemble les renseignements obtenus.

Θ_1 désigne la température de début de déshydratation d'un chélate hydraté, Θ_2 la température de début de pyrolyse du chélate anhydre.

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TABLEAU II

Phényl-oxinates	*Couleur*	*Températures*		*Perte de poids (%) totale*		*Perte de poids (%) par déshydratation*	
		Θ_1 °C	Θ_2 °C	*Expérimentale**	*Théorique*	*Expérimentale*	*Théorique*
$Cu(PhOx)_2$ $2H_2O$	Noir verdâtre	45	215	84.7	85.3	6.75*	6.67
				85.3	,,	7.9	,,
				85.3	,,	7.5	,,
$Zn(PhOx)_2$ anh.	Jaune vif	—	330	83.5	83.9	—	—
				84.6	,,	—	—
				84.8	,,	—	—
$Cd(PhOx)_2$ $1H_2O$	Jaune foncé	45	335	78.0	77.5	3.3	3.15
$Ni(PhOx)_2$ $1H_2O$	Jaune foncé	95	310	85.7	85.6	3.9	3.48
				84.8	,,	3.35	,,
				85.3	,,	—	,,
$Co(PhOx)_2$ $1H_2O$	Brun jaune**	95	295	84.4	84.5	3.75	3.48
				84.4	,,	4.1	,,
$Pb(PhOx)_2$ $2H_2O$	Jaune	50	295	67.5	67.35	5.25	5.27
$Hg(PhOx)_2$ anh.	Jaune orange	—	175	100	66.2	—	—
$Mn(PhOx)_2$ $1H_2O$	Brun clair	60	315	—	—	3.7	3.51
$MoO_2(PhOx)_2$ anhydre	Jaune	—	300	75.6	74.7	—	—
$Tl(PhOx)_3$ $1H_2O$	Orange	50	190	75.7	76.8	2.0	2.04

* Par pesée. Toutes les autres valeurs ont été mesurées sur le papier photographique.
** Nuance très variable.

TABLEAU III

Chélate	*Perte (%) par déshydratation*		*Nombre de moles H_2O*	Θ_1 °C	*Perte (%) par décomposition du chélate anhydre*		Θ_2 °C	*Mode de préparation*
	Observée	*Calculée*			*Observée*	*Calculée*		
$Cd(MeOx)_2$	0	—	0	—	70.15	70.05	310	a, b
$Mn(MeOx)_2$	4.55	4.62	1	125	78.4	78.7	295	c
$HgOx_2$(?)	0	—	0	—	100	—	130	a, b
$Hg(MeOx)_2$ (?)	3.5	3.4	1	45	100	—	$\sim$120	c
$PbOx_2$	6.9	6.8	2	45	55.6	55.0*	280	b
,,	3.9	3.5	1	130	57.9	58.2**	285	c
,,	0	—	0	—	59.2	,,	285	a
$Pb(MeOx)_2$	4.3	3.33	1.3	45	58.4	57.4*	275	b
,,	4.3	pour $1H_2O$	1.3	45	58.3	—	275	c
,,	4.2		1.3	55	57.5	60.2**	280	a

* Calculé pour PbO.
** Calculé pour Pb.
Le produit résiduel était tantôt PbO, tantôt Pb métal qui se réoxyde lentement.

a. Produit préparé à chaud selon le mode opératoire utilisé par BORREL ET PÂRIS[4].
b. Produit préparé et filtré à froid, et séché par aspiration d'un courant d'air.
c. Mode de préparation intermédiaire: précipitation à 60-70°. Dans tous les cas, le milieu était tamponné à l'acétate d'ammonium.

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III. CONCLUSIONS

Nos conclusions se présentent sous forme de tableaux ou de graphiques, où seront rassemblés les résultats de cette étude sur les phényl-2 oxinates et de celles déjà citées sur les oxinates et méthyl-2 oxinates, ces dernières étant d'ailleurs complétées par les résultats que nous présentons dans le Tableau III.

Le Tableau IV indique le nombre de molécules d'eau fixées sur chacun des chélates étudiés.

TABLEAU IV

Nombre de molécules H_2O	Al^{+3}	Mg^{+2}	Ni^{+2}	Co^{+2}	Zn^{+2}	Cd^{+2}	Cu^{+2}	Mn^{+2}	Hg^{+2}	Pb^{+2}	Tl^{+3}	Mo
Oxinates	0	2	2	2	2	2	2	2	0	0 à 2	1	$\frac{1}{2}$
Méthyloxinates	NC*	1	1	1	1	0	1	1	1	1,3	0	1/8
Phényloxinates	NC	NC	1	1	0	1	2	1	0	2	1	0

* NC: Ne donne pas de chélate.

Les températures Θ_1 de début de déshydratation et Θ_2 de début de décomposition des chélates des 3 réactifs sont portées sur les graphiques des Figs. 5 et 6. Les conclusions sont évidentes. Ainsi on notera que, sauf pour Hg, Pb et Tl, les chélates des deux dérivés substitués sont moins stables que les oxinates correspondants. Doit-on en conclure que l'accroissement de sélectivité obtenu en introduisant des substituants sur la molécule du réactif se paye par une perte de stabilité des chélates? Peut-être si l'on considère la stabilité thermique (résistance à la pyrolyse); mais cette stabilité thermique ne présente pas avec la stabilité ionique (dissociation en ions) une relation

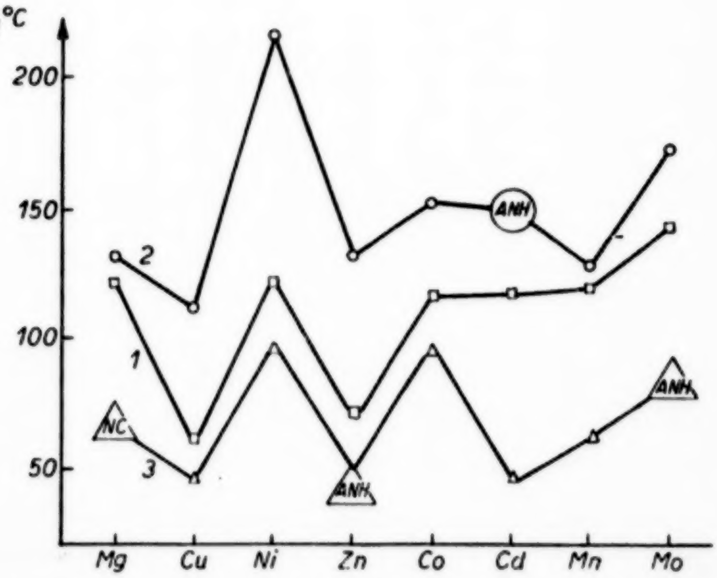

Fig. 5. Températures Θ_1 de déshydratation des chélates.
Courbe 1: oxinates; courbe 2: méthyloxinates; courbe 3: phényl-2-oxinates.

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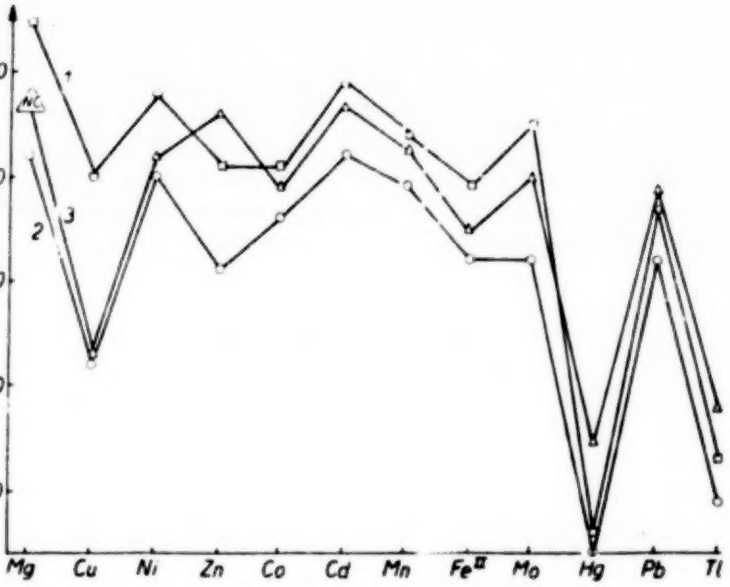

Fig. 6. Températures Θ_2 de début de décomposition des chélates.
Courbe 1: oxinates; courbe 2: méthyl-2-oxinates; courbe 3: phényl-2-oxinates.

évidente. A ce sujet, la confrontation des divers résultats reproduits ci-dessus nous donnera l'occasion d'une remarque intéressante.

On sait qu'il existe une série des stabilités ioniques, valable pour les chélates de nombreux réactifs. Cette série, qui a été établie également dans le cas des oxinates[7,8] et des méthyl-2 oxinates par JOHNSTON ET FREISER[8], est la suivante (stabilités décroissantes): Hg > Cu > Ni > Pb > Zn et Co > Cd > Fe^{II} > Mn > Mg > Ca (a).

Or, si l'on effectue un classement analogue avec les stabilités thermiques des oxinates, méthyl-2 et phényl-2 oxinates, on obtient 3 séries dont la moyenne est (stabilités croissantes):

Hg < Cu < Fe^{II} < Pb < Zn < Co < Mn < Ni < Cd < Mg (b).

Les séries (a) et (b) sont inverses: la stabilité thermique croît cependant que la stabilité ionique décroit.

Quel que soit le nombre d'exceptions que comporte chaque série particulière par rapport aux séries générales (a) et (b) — ces exceptions pouvant d'ailleurs être intéressantes à examiner de près — et en nous limitant à l'allure générale des phénomènes, nous pensons pouvoir affirmer que les chélates de l'oxine et de ses dérivés dont la stabilité ionique est la plus grande sont en général ceux qui résistent le moins bien à la pyrolyse.

RÉSUMÉ

Les auteurs ont étudié par potentiométrie les conditions de précipitation des phényl-2 oxinates, en milieu hydroalcoolique. Par analyse thermogravimétrique, ils ont ensuite déterminé le taux d'hydratation et les domaines de stabilité thermique de ces chélates. Ces résultats ont été comparés en outre avec ceux obtenus antérieurement pour les oxinates et les méthyl-2 oxinates.

SUMMARY

The authors have studied the potentiometric curves obtained during the neutralization, in dilute alcoholic media, of acid solutions containing 2-phenyl-8-quinolinol and metallic cations, with sodium hydroxide. By thermogravimetric analysis the number of water molecules and regions of stability for hydrates and anhydrous compounds were also established.

Moreover these results were compared with those previously obtained for oxinates and methyl-2 oxinates.

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ZUSAMMENFASSUNG

Die Verfasser haben die Neutralisation mit Natriumhydroxyd von 2-Phenyloxin, in saurer hydroalkoholischer Lösung und in Anwesenheit von Kationen, potentiometrisch verfolgt.

Mit Hilfe der thermogravimetrischen Analyse haben sie den Wassermolekülgehalt sowie die Temperaturgrenzen innerhalb derer die Hydrate und wasserfreien Verbindungen beständig sind, festgestellt. Diese Resultate wurden unter anderem mit denjenigen verglichen, die man früher für Oxinate und 2-Methyloxinate erhalten hatte.

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STUDIES ON NESSLER'S REAGENT AND NESSLER'S PRECIPITATE
PART II

by

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For the detection of ammonia, NESSLER[1] first introduced a reagent, the preparation of which has subsequently been modified by different workers[2] — the presence of $[\mathrm{HgI_4}]^{-2}$ ions being varied from 0.08*M* to 0.1*M* and the concentration of caustic alkalies from 0.5*M* to 3*M*. The existence of an intermediate compound has been shown in our previous communication[3].

The composition of the characteristic brown precipitate, formed when the Nessler's reagent is treated with ammonia, has been described in the literature as $\mathrm{NHg_2I,H_2O}$ by some workers[4] and as $\mathrm{NH_2Hg_2I_3}$ by others[5]. In our present communication attempts have been made to arrive at a definite conclusion regarding its composition from potentiometric study, assuming that the formation of the precipitate takes place in the following manner:

$$[\mathrm{HgI_4}]^{-2} + 2\ \mathrm{OH^-} \rightleftharpoons [\mathrm{Hg}\,{}^{(\mathrm{OH})_2}_{\mathrm{I}_2}]^{-2} + 2\mathrm{I^-} \tag{1}$$

$$2[\mathrm{Hg}\,{}^{(\mathrm{OH})_2}_{\mathrm{I}_2}]^{-2} + \mathrm{NH_3} \rightleftarrows \mathrm{NH}_{n-1}\mathrm{Hg_2I}_n,\mathrm{aq.} + (4\text{-}n)\mathrm{I^-} + n\mathrm{OH^-} \tag{2}$$

Now if the initial molar concentration of $[\mathrm{HgI_4}]^{-2}$ ions used be A, then,

$$A = A_1 + A_2 + 2A_3 \tag{3}$$

where A_1 and A_2 are the ultimate concentrations of $[\mathrm{HgI_4}]^{-2}$ and $[\mathrm{Hg}\,{}^{(\mathrm{OH})_2}_{\mathrm{I}_2}]^{-2}$ ions respectively and A_3 the number of moles of $\mathrm{NH}_{n-1}\mathrm{Hg_2I}_n$,aq. precipitated from a litre of the Nessler's solution, due to addition of a known amount of ammonia, the concentration of which is denoted by a. Throughout the series of an experiment, the concentration (B) of potassium hydroxide has been assumed to remain constant as it was present in large excess. So the apparent equilibrium constant K' from (1) is given by,

$$K' = \frac{A_2 I^2}{A_1} \tag{4}$$

where I is the concentration of total iodide ion liberated.
And from (1) and (2), we have,

$$I = 2A_2 + (8\text{-}n)A_3 \tag{5}$$

As $NH_{n-1}Hg_2I_n$.aq. is practically insoluble and ammonia remaining unreacted is infinitely small, it can be deduced from (2),

$$A_3 = a. \tag{6}$$

From (3), (4), (5) and (6) by solving, the expression for n is given by,

$$n = 8 - \frac{1}{a}\left\{ I - \frac{2(A - 2a)}{1 + \frac{I^2}{K'}} \right\} \tag{7}$$

EXPERIMENTAL

The values of I, with or without addition of ammonia to the Nessler's reagent, were calculated from the observed e.m.f. of the concentration cells containing iodide-hypoiodite system, following similar procedure and using the reagents of the same grade as described in detail in our previous communication. The concentration of iodide ion in the reference cell was 0.02M. It was observed that when caustic alkalies of high concentration were present in the Nessler's reagent, there was a deposition of yellow HgO at the liquid junction of the KCl bridge during e.m.f. measurements. This difficulty had been avoided by replacing KCl in the bridge with KOH, the concentration of which was the same as that of the alkali present in the concentration cells, and the observed e.m.f. values were corrected as usual. In each case, knowing the value of I before adding ammonia, K' was calculated from the relation (4) and from the corresponding value of I, after adding a known amount of ammonia, n in (7) was evaluated. The results are stated in Table I. The amount of ammonia was added in such a proportion as to precipitate 16% of mercury initially present in the solution.

TABLE I

CONCENTRATION OF IODIDE ION IN THE REFERENCE CELL = 0.02M

Concn. of $[HgI_4]^{-2}$ A	*Concn. of alkali* B	*E (corrected) in Volts* *Without ammonia*	*With ammonia*	*Concn. of ammonia* a	$p_A - 2p_B$	n
0.05	3.03	0.0140	0.0165	0.004	2.26	0.8
0.10	3.03	0.0195	0.0225	0.008	1.96	1.0
0.20	3.03	0.0245	0.0285	0.016	1.66	1.2
0.05	2.02	0.0130	0.0155	0.004	1.91	1.0
0.10	2.02	0.0175	0.0210	0.008	1.61	1.1
0.20	2.02	0.0230	0.0275	0.016	1.31	1.3
0.05	1.00	0.0100	0.0130	0.004	1.30	1.3
0.10	1.00	0.0150	0.0190	0.008	1.00	1.5
0.20	1.00	0.0220	0.0265	0.016	0.70	1.8
0.05	0.49	0.0070	0.0105	0.004	0.68	1.8
0.10	0.49	0.0120	0.0165	0.008	0.38	2.3
0.20	0.49	0.0205	0.0245	0.016	0.08	2.9

From the experimental data, it has been observed that n is a function of both A and B. In order to find out any empirical relation between n, A and B, a curve (Fig. 1) has been obtained by plotting n against the corresponding values of ($p_A - 2p_B$) and the following empirical relation has been derived,

$$n\ (\log_{10} \frac{B^2}{A} + 1) = 3.$$

Another set of experiments was carried out by adding the different amounts of ammonia to the same solution of Nessler's reagent and the results are stated graphically in Fig. 2, by plotting n against logarithm of the percentage of mercury precipitated as ammoniated product. It has been found that the value of n increases with the increase in concentration of ammonia. The colour of the precipitate also deepens

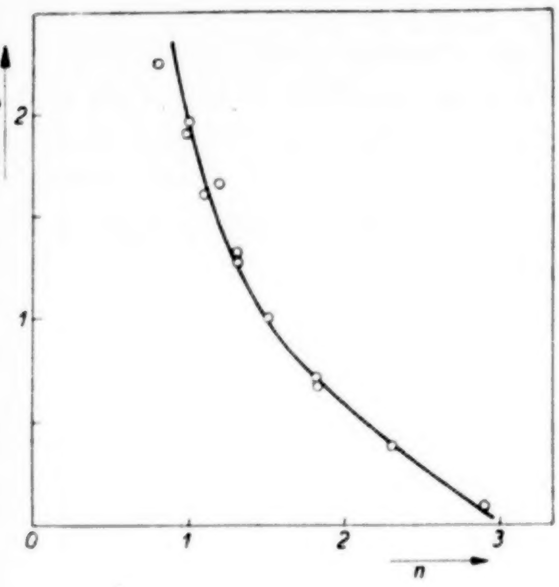


Fig. 1.

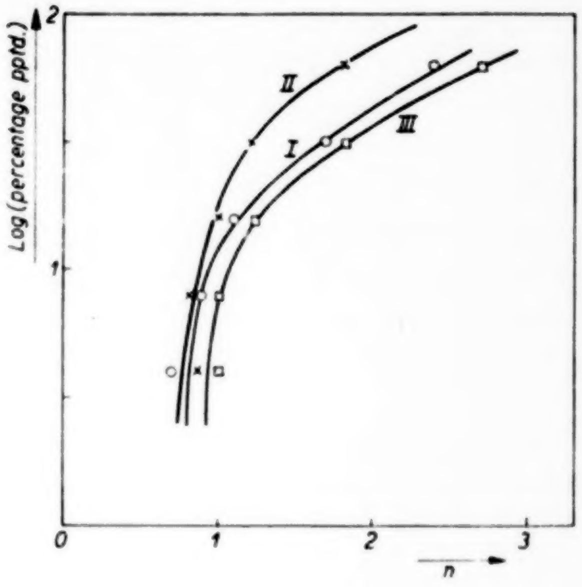
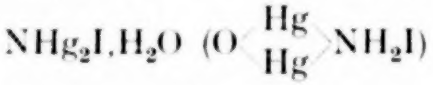


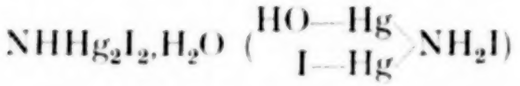
Fig. 2.
I — A = 0.1 *M*; B = 2.01 *M*
II — A = 0.1 *M*; B = 3.0 *M*
III — A = 0.2 *M*; B = 3.01 *M*

from brown to chocolate with the increase in iodine content and the chance of the formation of a precipitate containing no iodine is very remote.

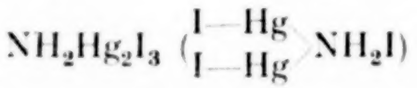
Hence it may be concluded that the composition of the precipitate depends on the concentrations of $[\mathrm{HgI_4}]^{-2}$ and $\mathrm{OH^-}$ ions as well as on the amount of ammonia added. The possible compositions are as stated below:



$\mathrm{NHg_2I{,}H_2O}\ \left(\mathrm{O}\left\langle\begin{matrix}\mathrm{Hg}\\ \mathrm{Hg}\end{matrix}\right\rangle\mathrm{NH_2I}\right)$ brown

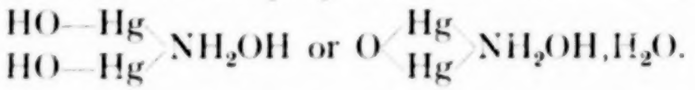


$\mathrm{NHHg_2I_2{,}H_2O}\ \left(\begin{matrix}\mathrm{HO{-}Hg}\\ \mathrm{I{-}Hg}\end{matrix}\right\rangle\mathrm{NH_2I}\Big)$ deep brown



$\mathrm{NH_2Hg_2I_3}\ \left(\begin{matrix}\mathrm{I{-}Hg}\\ \mathrm{I{-}Hg}\end{matrix}\right\rangle\mathrm{NH_2I}\Big)$ chocolate.

It may be of interest to recall the properties of Millon's Base[6]:



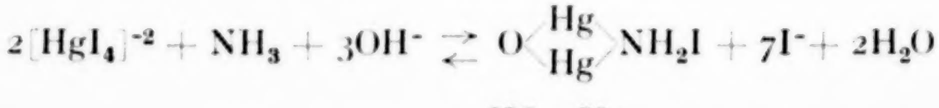
$$\left.\begin{matrix}\mathrm{HO{-}Hg}\\ \mathrm{HO{-}Hg}\end{matrix}\right\rangle\mathrm{NH_2OH}\ \text{or}\ \mathrm{O}\left\langle\begin{matrix}\mathrm{Hg}\\ \mathrm{Hg}\end{matrix}\right\rangle\mathrm{NH_2OH{,}H_2O}.$$

Ordinary salt solutions + Millon's Base → Salts of Millon's Base (very difficultly soluble) + hydroxide of metal, *e.g.*

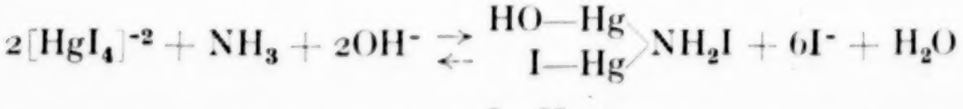
(i) Dilute KI solution + Millon's Base → Iodide of Millon's base + KOH, the filtrate being free from iodide ion.

(ii) $\mathrm{CuSO_4}$ or $\mathrm{FeCl_3}$ solution shaken with Millon's Base gives rise to a filtrate free from all salts.

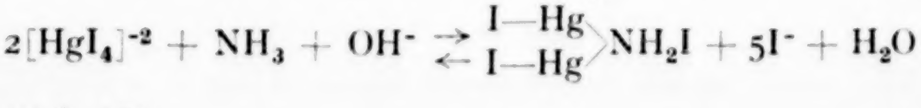
Therefore the suggested overall reactions are:

1) 

$$2[\mathrm{HgI_4}]^{-2} + \mathrm{NH_3} + 3\mathrm{OH^-} \rightleftarrows \mathrm{O}\left\langle\begin{matrix}\mathrm{Hg}\\ \mathrm{Hg}\end{matrix}\right\rangle\mathrm{NH_2I} + 7\mathrm{I^-} + 2\mathrm{H_2O}$$

2) 

$$2[\mathrm{HgI_4}]^{-2} + \mathrm{NH_3} + 2\mathrm{OH^-} \rightleftarrows \left.\begin{matrix}\mathrm{HO{-}Hg}\\ \mathrm{I{-}Hg}\end{matrix}\right\rangle\mathrm{NH_2I} + 6\mathrm{I^-} + \mathrm{H_2O}$$

3) 

$$2[\mathrm{HgI_4}]^{-2} + \mathrm{NH_3} + \mathrm{OH^-} \rightleftarrows \left.\begin{matrix}\mathrm{I{-}Hg}\\ \mathrm{I{-}Hg}\end{matrix}\right\rangle\mathrm{NH_2I} + 5\mathrm{I^-} + \mathrm{H_2O}$$

From the experimental data it may be observed that as the concentration of ammonia or iodomercurate ion increases, alkali remaining constant, the precipitate tends towards the formula $NH_2Hg_2I_3$; while when alkali concentration increases and the other reactants are constant, the formula of the precipitate approaches to NHg_2I, H_2O.

As the Nessler's reagent is mainly used for the detection or estimation of traces of ammonia, so it may be stated that the characteristic brown coloration or precipitation is due to the formation of NHg_2I,H_2O.

SUMMARY

The composition of the precipitate formed when the Nessler's reagent is treated with ammonia, is assumed as $NH_{n-1}Hg_2I_n$, aq. and has been studied potentiometrically from iodide-hypoiodite-system. It has been observed that the value of *n* depends on the concentrations of $[HgI_4]^{-2}$ and OH^- ions as well as on the amount of ammonia added and it may vary from 1 to 3. The colour of the precipitate deepens from brown to chocolate as the value of *n* increases.

RÉSUMÉ

Les auteurs attribuent au précipité, formé lorsque le réactif de Nessler est traité par l'ammoniaque, la formule suivante $NH_{n-1}Hg_2I_n$,aq. La formation de ce composé a été étudiée potentiométriquement à partir du système iodure-hypoiodite. On a constaté que la valeur de *n* dépend des concentrations des ions $[HgI_4]^{-2}$ et OH^-, ainsi que de la quantité d'ammoniaque ajoutée; elle peut varier de 1 à 3. La coloration du précipité fonce du brun au chocolat lorsque la valeur de *n* croît.

ZUSAMMENFASSUNG

Die Autoren geben dem Niederschlag, welcher sich bildet wenn man das Nesslersche Reagenz mit Ammoniak behandelt, folgende Formel: $NH_{n-1}Hg_2J_n$,aq. Die Bildung dieser Verbindung wurde potentiometrisch vom System Jodid-Hypojodit ausgehend untersucht. Man stellte fest, dass der Wert *n* von den Konzentrationen der Ionen $[HgJ_4]^{-2}$ und OH^-, sowie auch von der Quantität des hinzugefügten Ammoniaks abhängt; er kann zwischen 1 und 3 variieren. Die Farbe des Niederschlages vertieft sich mit wachsendem Wert von *n* von braun zu schokoladebraun.

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VOLUMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS
VII. REDUCTION WITH FERROUS ETHYLENEDIAMINE SULPHATE CERIC SULPHATE METHOD*

by

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CARAWAY AND OESPER[1] showed that ferrous ethylenediamine sulphate $FeSO_4 \cdot (CH_2.NH_3)_2SO_4 \cdot 4H_2O$ reacted stoichiometrically with standard solutions of three powerful oxidizing agents, namely, potassium permanganate, potassium dichromate and ceric sulphate which are commonly employed in oxidimetric titrations.

SINGH[2] *et al.* have used ferrous ethylenediamine sulphate for the indirect volumetric estimations of potassium chlorate, potassium bromate, potassium metaperiodate, potassium dichromate, potassium ferricyanide, potassium permanganate, potassium persulphate, hydrogen peroxide and ceric sulphate. The excess of ferrous ethylenediamine sulphate added to each of the substances was titrated with standard potassium permanganate and also with standard potassium dichromate solution. In the present investigation the substances have been determined indirectly by a volumetric method using ferrous ethylenediamine sulphate as reducing agent. The excess of standard ferrous ethylenediamine sulphate solution added to each of the substances was titrated with standard ceric sulphate solution using ferroin as an indicator.

EXPERIMENTAL

A known weight of each substance was mixed with an excess of standard ferrous ethylenediamine sulphate solution and the mixture acidified with sulphuric acid to keep its normality between 1 and 2*N*. In the case of potassium chlorate and potassium bromate the normality of the mixture with respect to sulphuric acid was kept between 4 and 6*N*. The mixture containing potassium chlorate was heated to 80° C for about ten minutes in an atmosphere of carbon dioxide and then allowed to cool. In the case of potassium ferricyanide, 5 ml of freshly prepared solution of ferric chloride (containing 1.0 g per 100 ml), 20 ml of 1*N* HCl, 30 ml of water and excess of ferrous ethylenediamine sulphate solution were added. The precipitate of $Fe_3[Fe(CN)_6]_2$ formed, was filtered and thoroughly washed with water. The filtrate, containing the excess of ferrous ethylenediamine sulphate, was acidified with sulphuric acid. In each case the excess of ferrous ethylenediamine sulphate was titrated against standard ceric sulphate solution using ferroin as an indicator.

All chemicals, except ceric sulphate, used in this investigation were of guaranteed purity. Ceric sulphate was standardized with A.R. arsenious oxide[3]. Ferrous ethylenediamine sulphate was prepared by the method of CARAWAY AND OESPER[1].

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* For Part VI of this series, see *Research Bull. Panjab Univ.*, (1955) 141.

The results given in Tables I to IX show that the substances can be determined indirectly by the volumetric method, using ferrous ethylenediamine sulphate (FES) as reducing agent in acid medium.

TABLE I

POTASSIUM CHLORATE

$KClO_3$ taken g	N/20 FES added ml	N/20 $Ce(SO_4)_2$ used for excess FES ml	N/20 FES used by $KClO_3$ ml	$KClO_3$ found g
0.0052	20.00	15.00	5.00	0.0051
0.0099	20.00	10.40	9.60	0.0098
0.0134	30.00	16.90	13.10	0.0133
0.0178	30.00	12.80	17.20	0.0176
0.0220	30.00	8.60	21.40	0.0219

TABLE II

POTASSIUM BROMATE

$KBrO_3$ taken g	N/20 FES added ml	N/20 $Ce(SO_4)_2$ used for excess FES ml	N/20 FES used by $KBrO_3$ ml	$KBrO_3$ found g
0.0068	20.00	15.00	5.00	0.0069
0.0138	20.00	10.00	10.00	0.0139
0.0207	30.00	15.00	15.00	0.0208
0.0276	30.00	10.00	20.00	0.0278
0.0346	45.00	20.00	25.00	0.0347

TABLE III

POTASSIUM METAPERIODATE

KIO_4 taken g	N/20 FES added ml	N/20 $Ce(SO_4)_2$ used for excess FES ml	N/20 FES used by KIO_4 ml	KIO_4 found g
0.0286	20.00	15.00	5.00	0.0287
0.0574	20.00	10.00	10.00	0.0575
0.0746	20.00	7.00	13.00	0.0747
0.0920	30.00	14.00	16.00	0.0920
0.1092	30.00	11.00	19.00	0.1092

TABLE IV

POTASSIUM DICHROMATE

$K_2Cr_2O_7$ taken g	N/20 FES added ml	N/20 $Ce(SO_4)_2$ used for excess FES ml	N/20 FES used by $K_2Cr_2O_7$ ml	$K_2Cr_2O_7$ found g
0.0123	30.00	25.05	4.95	0.0121
0.0240	30.00	20.10	9.90	0.0243
0.0339	30.00	16.10	13.90	0.0341
0.0416	30.00	13.00	17.00	0.0417
0.0487	30.00	10.05	19.95	0.0489

References p. 216

TABLE V

POTASSIUM FERRICYANIDE

$K_3[Fe(CN)_6]$ *taken* *g*	*N/20 FES* *added* *ml*	*N/20* $Ce(SO_4)_2$ *used for excess FES* *ml*	*N/20 FES* *used by* $K_3[Fe(CN)_6]$ *ml*	$K_3[Fe(CN)_6]$ *found* *g*
0.0548	10.00	5.00	5.00	0.0549
0.1096	20.00	10.00	10.00	0.1097
0.1425	30.00	17.00	13.00	0.1426
0.1754	30.00	14.00	16.00	0.1756
0.2083	40.00	21.00	19.00	0.2085

TABLE VI

POTASSIUM PERMANGANATE

$KMnO_4$ *taken* *g*	*N/20 FES* *added* *ml*	*N/20* $Ce(SO_4)_2$ *used for excess FES* *ml*	*N/20 FES* *used by* $KMnO_4$ *ml*	$KMnO_4$ *found* *g*
0.0078	20.00	15.00	5.00	0.0079
0.0156	20.00	10.00	10.00	0.0158
0.0204	20.00	7.00	13.00	0.0205
0.0252	25.00	9.00	16.00	0.0253
0.0300	35.00	16.00	19.00	0.0300

TABLE VII

POTASSIUM PERSULPHATE

$K_2S_2O_8$ *taken* *g*	*N/20 FES* *added* *ml*	*N/20* $Ce(SO_4)_2$ *used for excess FES* *ml*	*N/20 FES* *used by* $K_2S_2O_8$ *ml*	$K_2S_2O_8$ *found* *g*
0.0337	20.00	15.00	5.00	0.0338
0.0674	20.00	10.00	10.00	0.0676
0.0877	20.00	7.00	13.00	0.0878
0.1080	20.00	4.00	16.00	0.1081
0.1281	25.00	6.00	19.00	0.1283

TABLE VIII

HYDROGEN PEROXIDE

H_2O_2 *taken* *g*	*N/20 FES* *added* *ml*	*N/20* $Ce(SO_4)_2$ *used for excess FES* *ml*	*N/20 FES* *used by* H_2O_2 *ml*	H_2O_2 *found* *g*
0.0042	20.00	15.00	5.00	0.0043
0.0084	20.00	10.00	10.00	0.0085
0.0126	20.00	5.00	15.00	0.0128
0.0170	30.00	10.00	20.00	0.0170
0.0213	45.00	20.00	25.00	0.0213

TABLE IX

CERIC SULPHATE

$Ce(SO_4)_2$ taken g	N/20 FES added ml	N/20 $Ce(SO_4)_2$ used for excess FES ml	N/20 FES used by $Ce(SO_4)_2$ ml	$Ce(SO_4)_2$ found g
0.0830	20.00	15.00	5.00	0.0831
0.1660	20.00	10.00	10.00	0.1661
0.2325	20.00	6.00	14.00	0.2326
0.2990	30.00	12.00	18.00	0.2990
0.3654	30.00	8.00	22.00	0.3654

SUMMARY

Ferrous ethylenediamine sulphate has been used as a reducing agent in acid medium for the indirect volumetric estimations of potassium chlorate, potassium bromate, potassium metaperiodate, potassium dichromate, potassium ferricyanide, potassium permanganate, potassium persulphate, hydrogen peroxide and ceric sulphate. The excess of ferrous ethylenediamine sulphate added to each of the substances in acid medium was titrated with standard ceric sulphate solution using ferroin as an indicator.

RÉSUMÉ

Le sulfate double de fer(II) et d'éthylènediamine a été utilisé comme réducteur en milieu acide, pour les dosages volumétriques indirects du chlorate, du bromate, du métaperiodate, du dichromate, du ferricyanure, du permanganate et du persulfate de potassium, du peroxyde d'hydrogène et du sulfate cérique. L'excès de réactif ajouté à chacune de ces substances est titré par une solution étalon de sulfate de cérium(IV) en milieu acide, en présence de ferroïne comme indicateur.

ZUSAMMENFASSUNG

Das Doppelsalz aus Eisen(II) und Äthylendiaminsulfat wurde in saurem Milieu als Reduktionsmittel verwendet für indirekte volumetrische Bestimmungen von Kaliumchlorat, -bromat, -metaperjodat, -bichromat, -ferricyanid, -permanganat und -persulfat, Wasserstoffperoxyd und Cersulfat. Der Überschuss des zu jeder dieser Substanzen zugegebenen Reagenzes wird mit einer Titerlösung von Cer(IV)sulfat in saurer Lösung in Gegenwart von Ferroïn als Indikator titriert.

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OXIDATIONS WITH ALKALINE PERMANGANATE USING MONOVALENT THALLIUM FOR THE BACK-TITRATION

II. DETERMINATION OF IODATE, IODIDE AND FERROCYANIDE

by

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In estimating iodate and iodide STAMM[1], HEREDIA[2] and SINGH[3] oxidized them with potassium permanganate in alkaline medium, and back-titrated the excess oxidant with formate. In this investigation, monovalent thallium was used as a substitute for sodium formate[4] and a study was made of the oxidation of the above materials and of ferrocyanide with alkaline permanganate.

EXPERIMENTAL

Solutions of the substances to be oxidized, (*viz.* iodide, iodate[5] and ferrocyanide[6]) were prepared from the AnalaR or recrystallized products. Their solutions were standardized according to recommended procedures[5,6].

The experimental technique is the same as previously described[7]. The reactions to be described below consist of:

(a) the direct oxidation of the reducing substance in alkaline solutions with $KMnO_4$,

(b) titration of $KMnO_4$ with the reducing material in presence or absence of Ba^{+2} ions,

(c) oxidation of the reductant with $KMnO_4$ and back-titration of excess oxidant with monovalent thallium.

RESULTS

I. Oxidation of iodate with alkaline permanganate

On titrating $KMnO_4$ with iodate in absence of Ba^{+2} ions, the reaction products are periodate and manganate. The inflection at the end-point is very poor, amounting

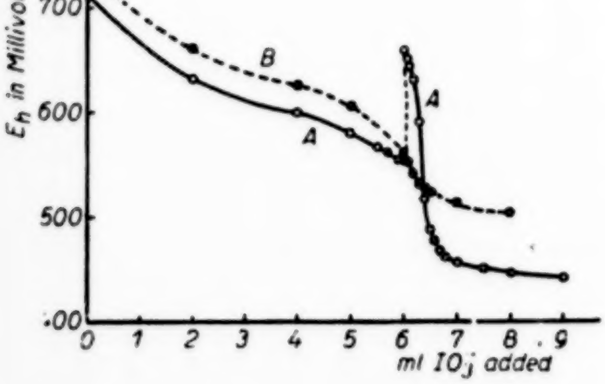

Fig. 1.

(A) 25 ml 0.1261 N $KMnO_4$, 2 N NaOH titrated with 0.0992 N IO_3^-, Ba^{+2} added just before end-point.

(B) Same as (A) with no Ba^{+2}.

to ∼ 12 mV in the presence of 3*N* NaOH (*cf.* Fig. 1 B). At lower alkalinity no apparent inflection was observed characterizing the end-point.

In the presence of Ba^{+2} ions on the other hand, the inflections are sharper amounting to ∼ 70–80 mV but the end-points are always attained late. This is possibly due to the precipitation of $Ba(IO_3)_2$ which escapes oxidation. The amount of the precipitated iodate apparently increases by increasing the concentration of Ba^{+2} present, leading to still later end-points. On slowly stirring the solution, the precipitated iodate settles down and the equilibria are rapidly attained. If on the other hand the stirring is vigorous, the time for equilibrium increases on account of the oxidation of the precipitated salt. Better results could be obtained by performing the titrations in 2*N* NaOH in the absence of Ba^{+2} ions, the latter being added only just before the end-point, when a sudden rise in potential occurs (*cf.* Fig. 1 A). On continuing the titration a sharp inflection is observed at the end-point. The latter deviates only slightly from the theoretical values when 0.1*N* solutions are used, but the deviation increases with dilution of the iodate solution.

TABLE I

TITRATION OF 25 ml 0.1261*N* $KMnO_4$ WITH IO_3^-

Alkalinity	*Vol. of 5% Ba^{+2}*	*Max. inflec. per 0.1 ml IO_3^-*	*Theor. end-point*	*Exptl. end-point*	*Error*
		$IO_3^- = 0.0992N$			
3*N* NaOH	—	12 mV	6.36 ml	6.15 ml	3.3 %
1.5*N*	6 ml	19	6.36	6.57	−3.3
1.5*N*	10	80	6.36	6.82	−7.27
2*N*	10 *	103	6.36	6.385	−0.39
2*N*	8 **	74	6.36	6.325	0.55
		$IO_3^- = 0.0496N$			
2*N*	10 ml ***	66 mV	12.72 ml	12.58 ml	1.1 %

* Ba^{+2} added 0.4 ml before end-point.
** Ba^{+2} added 0.1 ml before end-point.
*** Ba^{+2} added 0.6 ml before end-point.

II. Oxidation of iodide

On titrating $KMnO_4$ with iodide, the latter is oxidized either to iodate or periodate, depending on whether Ba^{+2} ions are absent or present. In presence of Ba^{+2} ions the end-points are attained with considerable jumps (*cf.* curve A, Fig. 2) which can be decreased by decreasing the concentrations of solutions and the quantity of Ba^{+2} present. As is apparent from the data shown in Table II, the results vary according to the concentration of the reactants, the errors amounting to 0.5–0.63% in case of the 0.1*N* solutions, and increase when the concentrations are lowered. In absence of Ba^{+2} ions a smaller jump is observed which corresponds to the oxidation of I^- to IO_3^- (curve B, Fig. 2), the periodate formed being possibly reduced by the titrant[8].

In both cases the reaction is slow, needing ∼ 5-10 min at the beginning and 30 min at the end-point. Attempts to accelerate the reaction by using HgO, ZnO, Ni^{+2}, and Au^{+3} ions were futile.

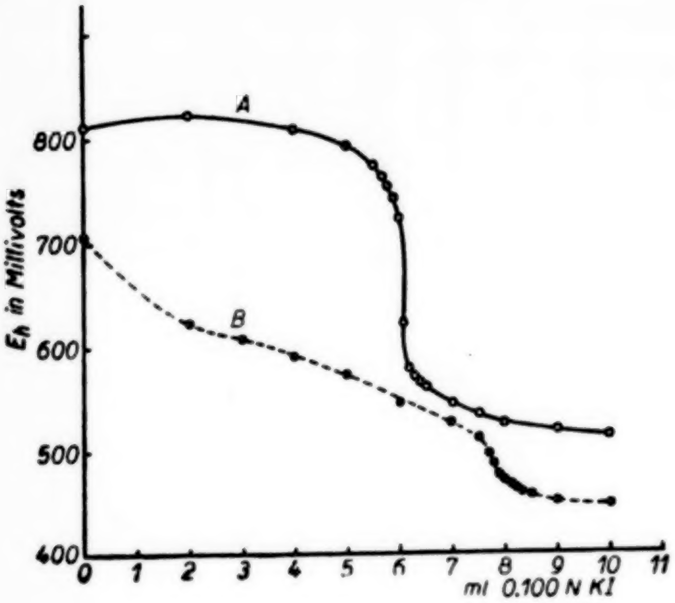

Fig. 2. Titration of 25 ml $0.1203N$ $KMnO_4$ with $0.1000N$ KI.
(A) $0.5N$ NaOH + Ba^{+2} ions
(B) $2N$ NaOH

In the direct titration of I^- with $KMnO_4$ in presence of Ba^{+2} ions a jump amounting to ∼ 70 mV is observed at the end-point, which corresponds to the oxidation of $I^- \rightarrow IO_3^-$. The errors in this case are considerable, ranging from 3-5% in 1-3N NaOH and the reaction is slower than the reverse titration of $KMnO_4$ with I^-.

TABLE II

TITRATION OF $KMnO_4$ WITH I^- IN PRESENCE OF Ba^{+2} IONS

Alkalinity	*Max. inflec. per 0.1 ml I^-*	*Vol. of 5% Ba^{+2}*	*Theor. end-point*	*Exptl. end-point*	*Error*
25 ml $0.1203N$ $KMnO_4$ titrated with $0.1N$ I^-:					
$1N$ NaOH	108 mV	10 ml	6.02 ml	6.05 ml	−0.5 %
$0.5N$	96	10	6.02	6.04	−0.33
25 ml $0.1261N$ $KMnO_4$ titrated with $0.05N$ I^-:					
$0.5N$ NaOH	62 mV	10 ml	12.62 ml	12.73 ml	−0.91
25 ml $0.02406N$ $KMnO_4$ titrated with $0.01N$ I^-:					
$1N$ NaOH	24 mV	3 ml	12.04 ml	11.35 ml	5.73
$0.5N$	16	3	12.04	11.9	1.16

TABLE III

TITRATION OF $KMnO_4$ WITH I_2-I^--MIXTURE

Alkalinity	*Vol. of 5% Ba^{+2}*	*Max. inflec. per 0.1 ml titrant*	*Theor. end-point*	*Exptl. end-point*	*Error*
25 ml of $0.1631N$ $KMnO_4$ titrated with $0.0822N$ I_2 + $0.05N$ I^-:					
$1N$ NaOH	–	18 mV	9.43 ml	9.48 ml	−0.53 %
$1N$	10 ml	59	7.07	7.065	0.07
$0.5N$	10	47	7.07	7.015	0.78
$0.5N$	10	50	7.07	7.06	0.14
$0.8N$	10	64	7.07	7.00	0.99

III. Oxidation of iodine in potassium iodide

As may be seen from the data shown in Table IV and Fig. 3, results similar to those found with iodide are obtained when a solution of I_2 in KI is used as the titrant. In presence of Ba^{+2} ions the oxidation of both ingredients yields IO_4^-, whereas in absence of Ba^{+2} they yield iodate. These reactions are somewhat more rapid than with the iodide alone, needing 5-6 min and 20 min at the beginning of the titration and at the end-point respectively.

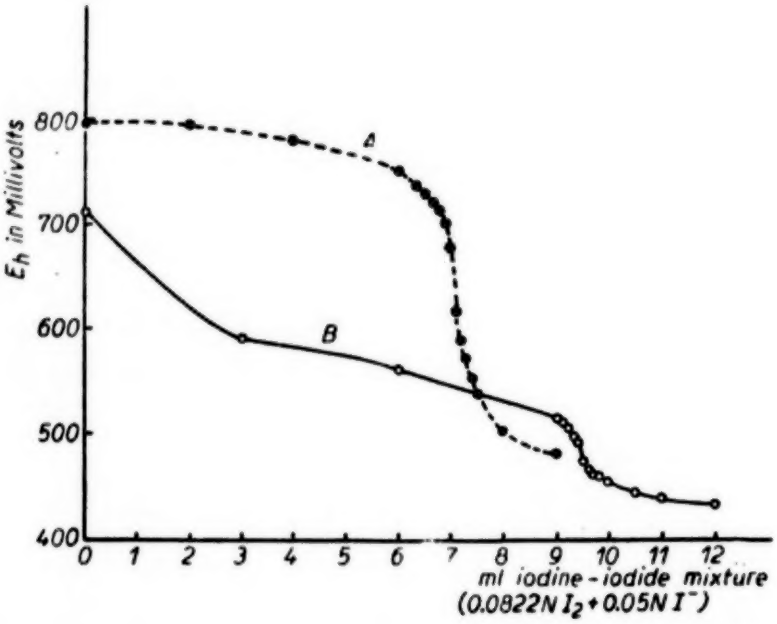

Fig. 3. Titration of 25 ml 0.1163N $KMnO_4$ in 1N NaOH with (0.0822N I_2 + 0.05N KI).
(A) in presence of Ba^{+2} ions
(B) in absence of Ba^{+2} ions

IV. Oxidation of ferrocyanide

In the oxidation of ferrocyanide with $KMnO_4$ in acid medium precipitation of manganous ferrocyanide occurs if the acid concentration is not sufficiently high, yielding inaccurate results[6]. It was thought that this difficulty could be overcome by performing the titrations in alkaline medium where reduction of $KMnO_4$ is checked at the MnO_2 stage. On titrating $K_4[Fe(CN)_6]$ solution free from acid or alkali the end-points are attained 1% earlier than the theoretical values. The errors increase on making the solution slightly acid but decrease on making it somewhat alkaline. Better results could be obtained in presence of telluric acid or sodium tellurate and 0.025-0.1N NaOH. At higher alkalinities than 0.1N, reduction of MnO_4^- yields MnO_4^{-2} without a characteristic inflection. The reaction is more or less rapid in absence of alkali but slows very much when alkali is added.

The titration curves (Fig. 4) are smooth but the inflections at the end-points are not very sharp, amounting to 20-30 mV per 0.1 ml $KMnO_4$.

Titration of $KMnO_4$ with ferrocyanide gives rise to manganate and contrary to the reverse process equilibria are rapidly attained. In absence of Ba^{+2} ions, the inflection at the end-point is not sharp but becomes distinct amounting to 50-80 mV in presence of Ba^{+2} ions (*cf.* Fig. 5).

The difficulty with this reaction is that the position of the end-point varies with the rate of adding the titrant (*cf.* Table IV A). However, satisfactory results could be obtained by slowly adding the titrant in presence of 0.5-1N NaOH and Ba^{+2} ions twice or 1½ times equivalent to the manganate formed in the reaction. However, the errors increase on decreasing the concentration of the reactants, owing perhaps to the partial dissociation of dilute ferrocyanide in the alkaline solution, whereby the free cyanide takes part in the reduction of $KMnO_4$. Larger errors were also observed when the ferrocyanide solution was prepared from the non-crystallized AnalaR samples.

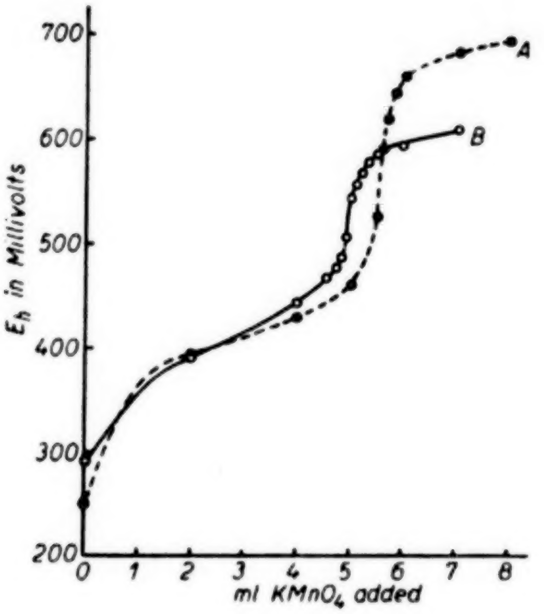

Fig. 4.

(A) Titration of 5 ml 0.0814*N* ferrocyanide, 0.05*N* NaOH + telluric acid with 0.1192*N* $KMnO_4$.
(B) Titration of 5 ml 0.0863*N* ferrocyanide, no alkali, with 0.1438*N* $KMnO_4$.

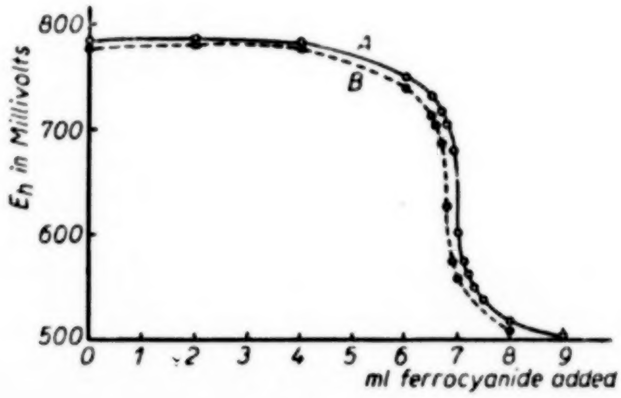

Fig. 5.

(A) Titration of 25 ml 0.1204*N* $KMnO_4$ with 0.0863*N* ferrocyanide in 1*N* NaOH + Ba^{+2} ions.
(B) Titration of 10 ml 0.1204*N* $KMnO_4$ with 0.0353*N* ferrocyanide, 1*N* NaOH + Ba^{+2} ions.

TABLE IV A

TITRATION OF 25 ml 0.1204*N* $KMnO_4$ WITH 0.0925 FERROCYANIDE IN PRESENCE OF Ba^{+2} IONS

Alkalinity	*Vol. of 5% Ba^{+2}*	*Rate of adding titrant*	*Max. inflec. at end-point*	*Theor. end-point*	*Exptl. end-point*	*Error*
0.5*N* NaOH	7 ml	slow	86 mV	6.5 ml	6.455 ml	0.69 %
0.5*N*	7	rapid	62	6.5	6.67	−2.62
1.5*N*	7	slow	64	6.5	6.36	2.15
1.5*N*	7	rapid	60	6.5	6.75	−1.15
1*N*	5	slow	50	6.5	6.44	0.92
1*N*	10	slow	61	6.5	6.47	0.42

TABLE IV B

TITRATION OF $KMnO_4$ WITH FERROCYANIDE (ADDED SLOWLY) IN PRESENCE OF Ba^{+2} IONS AND 1N NaOH

Vol. and Normality of $KMnO_4$	*Normality of ferrocyanide*	*Vol. of 5% Ba^{+2}*	*Max. inflec. per 0.1 ml titrant*	*Theor. end-point*	*Exptl. end-point*	*Error*
25 ml 0.1204N	0.0863	7 ml	80 mV	6.98 ml	6.955 ml	0.36 %
25 ml 0.12 4N	0.0706	7	69	8.53	8.54	−0.12
10 ml 0.1204N	0.0353	7	58	6.82	6.79	0.44
25 ml 0.02408N	0.0212	2	60	5.68	5.58	1.76
25 ml 0.02408N	0.01412	2	21	8.53	8.23	3.52

TABLE V

TITRATION OF FERROCYANIDE WITH PERMANGANATE

Acidity or Alkalinity	*Max. inflec. per 0.1 ml $KMnO_4$*	*Theor. end-point*	*Exptl. end-point*	*Error*
5 ml 0.0746N $K_4[Fe(CN)_6]$ diluted twice and titrated with 0.1192N $KMnO_4$:				
$1.5 \cdot 10^{-1}N$ H_2SO_4	27 mV	5.22 ml	5.04 ml	−3.45 %
$1.5 \cdot 10^{-4}N$	31	5.22	5 06	−3.07
$1.5 \cdot 10^{-6}N$	25	5.22	5.14	−1.35
$1.5 \cdot 10^{-7}N$	27	5. 2	5.15	−0.96
— (aqueous)	27	5.22	5.15	−0.96
5 ml 0.0814N $K_4[Fe(CN)_6]$ diluted twice and titrated with 0.1192N $KMnO_4$:				
0.05N NaOH	16 mV	5.69 ml	5.63 ml	−1.05 %
0.025N NaOH + telluric acid	29	5.69	5.65	−0.7
0.1N NaOH	27	5.69	5.734	0.77
0.025N NaOH + sodium tellurate ($KMnO_4$ = 0.1246N)	20	5.44	5.46	0.37

V. Oxidation with permanganate and back-titrating excess oxidant with monovalent thallium

The process consists in the oxidation of a given volume of the substance to be estimated by a known excess of $KMnO_4$ in presence of 1N NaOH and Ba^{+2} ions equivalent to the permanganate present.

The excess $KMnO_4$ is then titrated with monovalent thallium. This latter reagent was preferred to formate and formic acid on account of the rapidity of its reaction with $KMnO_4$.

In the estimation of iodate by mixing with $KMnO_4$ in 1N NaOH and in presence of Ba^{+2} ions erroneous results were obtained, apparently due to partial precipitation of $Ba(IO_3)_2$ which escapes oxidation. Better results can be obtained when the oxidation of the iodate is performed in absence of Ba^{+2} ions, the latter being added just before titrating excess $KMnO_4$ with Tl^+.

In trying to determine the excess of $KMnO_4$ after oxidizing ferrocyanide with formic acid, the reaction was very slow and the errors considerable. Tl^+ was therefore applied and the reaction then occurred rapidly. Good results can be obtained if the excess $KMnO_4$ is back-titrated immediately after mixing.

From the above study it becomes apparent that oxidation of iodate, iodide and iodine with permanganate is beset with many difficulties on account of the following facts:

(a) the smallness of the inflections in absence of Ba^{+2} ions,
(b) the precipitation of $Ba(IO_3)_2$ when Ba^{+2} ions are added,
(c) the tendency of I^- to give different oxidation products, *viz.* IO_3^- and IO_4^-.

Further studies will be made in an attempt to overcome these difficulties.

TABLE VI

Vol. of reductant added	*Theor. end-point*	*Exptl. end-point*	*Error*
25 ml 0.1291*N* $KMnO_4$ mixed with 0.0992*N* IO_3^-, and excess oxidant titrated with 0.0369*N* Tl^+:			
3 ml IO_3^-*	9.46 ml	10.06 ml	−6.34 %
3 **	9.46	9.55	−0.95
3 **	9.46	9.54	−0.85
25 ml 0.1294*N* $KMnO_4$ mixed with 0.1*N* I^-, and excess oxidant titrated with 0.0369*N* Tl^+:			
3 ml I^-	9.40 ml	9.34 ml	0.64 %
25 ml 0.1246*N* $KMnO_4$ mixed with 0.0814*N* $[Fe(CN)_6]^{-4}$, and excess oxidant titrated with 0.0369*N* Tl^+:			
5 ml $[Fe(CN)_6]^{-4}$	5.83 ml	5.825 ml	0.09 %
5	5.83	5.872	−0.77
3	10.25	10.2	0.49
1	14.67	14.72	−0.34
5 ***	5.83	5.735	1.63

* Ba^{+2} added from beginning.
** Ba^{+2} added after mixed with iodate, oxidant titrated immediately after mixing.
*** Titration of oxidant half-an-hour after mixing.

SUMMARY

Iodate, iodide, iodine and ferrocyanide can be estimated by oxidation with $KMnO_4$ in alkaline media; the excess is back-titrated with Tl^7. I^- and I_2 are oxidized to IO_4^- in the presence of Ba^{+2} ions but only to IO_3^- in absence of such ions. The direct titration of IO_3^-, I^- with $KMnO_4$ proved valueless.

Ferrocyanide is oxidized by $KMnO_4$ in alkaline solutions and MnO_2 is formed. In the presence of telluric acid and 0.025-0.1*N* NaOH satisfactory results are obtained. Reduction of MnO_4^- with ferrocyanide gives MnO_4^{-2} and the results are variable, depending on the rate of adding the ferrocyanide.

RÉSUMÉ

Les iodates, iodures, ferrocyanures et l'iode peuvent être dosés par oxydation au moyen de $KMnO_4$, en milieu alcalin; on titre l'excès de permanganate par le thallium(I). I^- et I_2 sont oxydés en iodate en l'absence de Ba^{+2}, et en periodate, en présence de Ba^{+2}. Dans le cas de l'oxydation des ferrocyanures, il y a formation de MnO_2. En présence d'acide tellurique, dans NaOH 0.025 à 0.1*N*, les résultats sont satisfaisants. Cependant, dans le cas de la réduction du $KMnO_4$ par les ferrocyanures, il y a formation de MnO_4^{-2}, les résultats dépendant de la vitesse d'addition du ferrocyanure.

ZUSAMMENFASSUNG

Die Jodate, Jodide, Ferrocyanide und das Jod können mittels einer Oxydation mit Hilfe von $KMnO_4$ in alkalischer Lösung bestimmt werden. Man titriert den Überschuss des Permanganates mit Thallium(I). J^- und J_2 werden in Abwesenheit von Ba^{+2} zu Jodat oxydiert und in Gegenwart

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von Ba^{+2} zu Perjodat. Im Falle der Oxydation der Ferrocyanide wird MnO_2 gebildet. Die Resultate sind in Gegenwart von Tellursäure in 0.025 bis 0.1*N* NaOH befriedigend. Im Falle der Reduktion des $KMnO_4$ durch Ferrocyanid dagegen, wird MnO_4^{-2} gebildet und die Ergebnisse hängen von der Zugabegeschwindigkeit des Ferrocyanides ab.

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BROMOMETRIC DETERMINATION OF VANADIUM(V) BY HYDRAZINE

by

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Reduction of vanadium(V) to vanadium(IV) by hydrazine sulphate in sulphuric acid was studied by HOFMANN AND KÜSPERT[1] and the method was adopted for the gasometric and oxidometric determination of hydrazine. It was found that hydrazine is oxidized by vanadium(V) to nitrogen and water according to equation (1).

$$4VO_3^- + 12H^+ + N_2H_4 \rightarrow 4VO^{+2} + N_2 + 8H_2O \quad \ldots\ldots\ldots \quad (1)$$

Later investigations of this reaction by BROWNE AND SHETTERLY[2] revealed the occurrence of a partial side reaction resulting in the formation of hydronitric acid and ammonia.

$$4VO_3^- + 12H^+ + 2N_2H_4 \rightarrow 4VO^{+2} + HN_3 + NH_3 + 8H_2O \quad \ldots \quad (2)$$

They observed that the extent of this side reaction depends on sulphuric acid concentration and temperature. The gasometric procedure gave an average negative error of about 4%, whereas the oxidometric procedure which consisted of the oxidation of vanadium(IV) formed by $KMnO_4$, showed an error of less than 1%. The reduction of the error in the latter case was attributed to the oxidation of hydronitric acid by $KMnO_4$. BRAY AND CUY[3] confirmed the above findings and discarded the use of vanadium(V) for the estimation of hydrazine.

In a study of the oxidation of hydrazine by bromate and permanganate KOLTHOFF[4] inferred that these reactions proceed smoothly according to equation (1) in sufficiently high concentration of hydrochloric acid, while the side reaction (2) occurs to some extent in dilute sulphuric acid. It seemed, therefore, that the occurrence of the side reaction in the reduction of vanadium(V) by hydrazine may be suppressed by maintaining high concentration of hydrochloric acid.

WILLARD AND YOUNG[5] described a method for determining vanadium in chromium-vanadium steels by preferential oxidation of vanadium(IV) in presence of Cr(III) by potassium bromate. In the actual procedure the solution of the sample (in sulphuric acid), containing 10-20 mg vanadium, is heated for 15 minutes at 50-60° C with 2 to 3 g of potassium bromate in presence of hydrochloric acid and ammonium sulphate. The excess bromate is destroyed by boiling the solution and vanadium(V), which is formed, is titrated against standard $FeSO_4$. Preliminary tests in these laboratories showed that the oxidation of vanadium(IV) by bromate was very slow at room temperature and that in mixed solution containing vanadium(IV) and hydrazine the latter could be preferentially titrated against bromate in hydrochloric acid medium.

The bromometric determination of vanadium(V) by hydrazine consisted, therefore, of the reduction of vanadium(V) by a known excess of hydrazine in presence of sufficient hydrochloric acid to vanadium(IV) and the titration of excess hydrazine against standard potassium bromate.

The dead-stop end-point procedure of Foulk and Bawden[6], because of the speed, accuracy and easy detection of the end-point, was adopted for the titration of hydrazine against potassium bromate, in place of the classical dyestuff indicator method[4].

EXPERIMENTAL

Stock solutions of vanadium(V) were prepared by accurately weighing out the requisite amount of vanadium pentoxide (E. Merck) and dissolving it in sodium carbonate (AnalaR). The vanadium content of an aliquot of the solution as determined by reduction of vanadium(V) by a known excess of $FeSO_4$, and back titration of the excess $FeSO_4$ against standard $Ce(SO_4)_2$ or $KMnO_4$ in high concentration of sulphuric acid, using ferroïn as indicator (*cf.* Willard and Young[7]) showed a close agreement with that calculated from the weight of vanadium pentoxide. Hydrazine sulphate solution was prepared by dissolving the necessary quantity of AnalaR sample in water. Its strength was determined by titration against standard $KBrO_3$ using the dead-stop end-point procedure.

Aliquot of vanadium(V) solution was taken in a 400 ml beaker, acidified with HCl and known excess of hydrazine sulphate solution was added to it. The overall acid normality was 4-5*N*. The solution was stirred and allowed to stand for 15 minutes. The dead-stop end-point titration unit was a simple manual type of apparatus with two identical platinum electrodes, a mechanical stirrer, and a sensitive galvanometer with adjustible shunt as employed by Foulk and Bawden *(loc. cit.)*. The potential applied across the electrodes was 10-20 millivolts. After adding about 2 g of potassium bromide to the mixed solution the stirrer was started and the excess hydrazine was titrated against standard $KBrO_3$. Sufficient hydrochloric acid was added to maintain the acidity above 4-5*N* as recommended by Kolthoff *(loc. cit.)*. The approach of the end-point was characterized by the temporary shift in the deflection of the galvanometer, with almost instantaneous return to the original position, after each addition of $KBrO_3$. The end-point was indicated by a sharp and permanent kick in the galvanometer deflection. The bromate equivalent of hydrazine added, was similarly determined. The difference of the two bromate titer values gave directly the amount of vanadium(V) in terms of standard $KBrO_3$. One ml of potassium bromate (0.1*N*) corresponds to 0.005095 g vanadium. The relation is based on the following considerations:

$$4VO_3^- + N_2H_4 + 12H^+ \rightarrow 4VO^{+2} + N_2 + 8H_2O$$
$$3N_2H_4 + 2BrO_3^- \rightarrow 3N_2 + 6H_2O + 2Br$$
$$\text{Thus } 2BrO_3^- \equiv 3N_2H_4 \equiv 12VO_3^-$$

Since the equivalent weight of bromate is 1/6 its molecular weight,
1 g equivalent of bromate $\equiv$ 1 g atom of vanadium.

Table I shows a typical set of results.

The close agreement between the observed and the calculated values for the vanadium content, substantiates the observation that under the given operative conditions vanadium(IV) is not oxidized by $KBrO_3$ and that the present method may therefore be adopted for the quantitative estimation of vanadium(V).

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TABLE I

Expt. No.	*Vol. of vanadium solution ml*	*Hydrazine added ml*	*$KBrO_3$ for excess hydrazine ml*	*$KBrO_3$ for hydrazine added ml*	*Normality of $KBrO_3$*	*Amount of vanadium g*		*Difference g*
						Found	*Taken*	
1	25	10	36.70	51.00	0.03863*N*	0.02814	0.02800	+0.00014
2	20	10	33.80	50.80	0.03863*N*	0.03345	0.03364	−0.00019
3	20	10	10.85	19.60	0.1000*N*	0.04457	0.04472	−0.00015
4	25	20	28.15	39.20	0.1000*N*	0.05628	0.05590	+0.00038
5	50	10	22.55	51.00	0.03863*N*	0.05600	0.05600	nil
6	40	10	16.50	50.80	0.03863*N*	0.06750	0.06726	+0.00024
7	75	10	8.65	51.00	0.03863*N*	0.08333	0.08400	−0.00067
8	50	20	14.45	36.50	0.1000*N*	0.1123	0.1118	+0.00050

Our sincere thanks are due to Professor S. S. Joshi for facilities and kind interest in the work.

SUMMARY

A method for the quantitative determination of vanadium(V), based on the reduction of vanadium(V) by hydrazine, has been described. The reduction is carried out in high concentration of hydrochloric acid and the excess hydrazine back-titrated against standard potassium bromate, using the dead-stop end-point procedure. Hydrazine is preferentially oxidized by bromate in presence of vanadium(IV). Accurate results have been obtained over a wide range of vanadium(V) concentration.

RÉSUMÉ

Une méthode de dosage du vanadium basée sur la réduction du vanadium(V) par l'hydrazine est décrite. Cette réduction est effectuée dans l'acide chlorhydrique en forte concentration; l'excès d'hydrazine est titré en retour par une solution étalon de bromate de potassium, par la méthode du "dead-stop". L'hydrazine s'oxyde, par le bromate, plus facilement que le vanadium(IV). Des résultats précis ont été obtenus pour des concentrations très différentes de vanadium(V).

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Vanadium beschrieben, welche auf der Reduktion des Vanadium(V) mit Hydrazin beruht. Diese Reduktion wird in stark konzentrierter Salzsäure ausgeführt. Der Überschuss an Hydrazin wird mit einer Vergleichslösung von Kaliumbromat nach der ,,dead-stop" Methode zurücktitriert. Das Hydrazin wird durch Bromat leichter oxydiert als Vanadium(IV). Es wurden genaue Resultate für sehr verschiedene Konzentrationen an Vanadium(V) erhalten.

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ANALYSIS OF STYRENATED METHYL ESTERS OF LINSEED OIL FATTY ACIDS BY MOLECULAR DISTILLATION

by

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INTRODUCTION

Though much attention has been paid in recent years to the reaction of styrene with drying oils, little is yet known about the nature of the reaction products. Most of the work done deals with the separation of high-molecular polystyrene from styrenated oils by precipitation methods. The lack of a method whereby a good separation of the reaction products can be effected without changing the nature of the products is one of the main difficulties.

PETIT AND FOURNIER[1] subjected the mixture of fatty acids which remained after the removal of polystyrene from styrenated linseed and tung oil to a distillation at pressures ranging from 2 to 5 mm Hg. They claimed the isolation of a fraction which contained one mole styrene per mole fatty acid which they supposed to be a Diels-Alder adduct (styrene reacting as a dienophile). As considerable cracking took place during the distillation, the determination of the styrene content based on determination of acid values is not reliable. Unstyrenated oils subjected to the same treatment gave fractions the acid values of which differed much from the original fatty acids.

A way to avoid the degradation of the products is the use of molecular distillation of the esters rather than normal vacuum distillation of the free acids.

EXPERIMENTAL PART

The molecular still used was of the cascade fractionating-type as described by ALDERSHOFF, BOOY, LANGEDIJK, PHILIPPI AND WATERMAN[2]. The high separating power is due to nine stages of vaporization and condensation. The still proper and the vacuum system were constructed as separate units, each unit being transportable to permit easier handling of the apparatus. The molecular still and the vacuum system are shown diagrammatically in Fig. 1. A photograph of the assembly is shown in Fig. 2.

Determination of the separating power

An idea of the separating efficiency was obtained by determining the plate number of the still using the data of BOOY *et al.*[2] who distilled a mixture of di-*n*-butyl phthalate and di-*n*-butyl

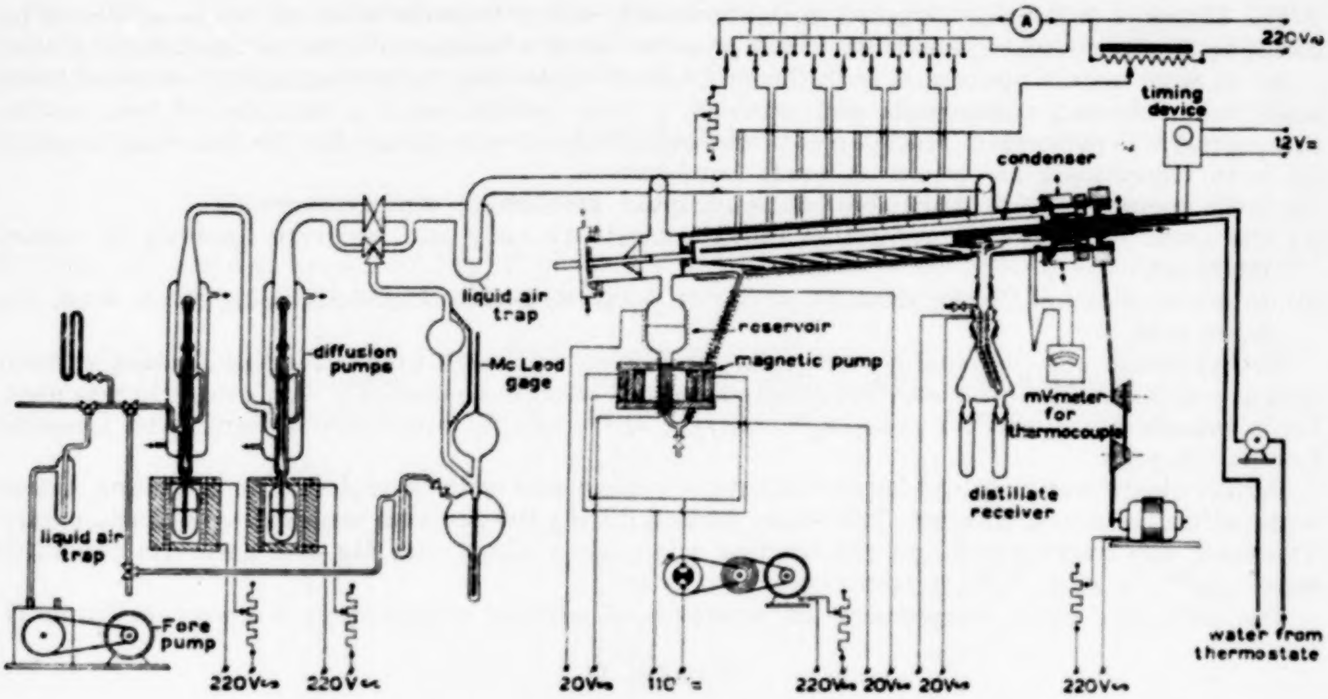
A
220V~
timing device
12V=
condenser
liquid air trap
diffusion pumps
Mc Leod gage
reservoir
magnetic pump
mV-meter for thermocouple
distillate receiver
liquid air trap
Fore pump
220V~
220V~
20V~
110 =
220V~
20V~
20V~
220V~
water from thermostate

Fig. 1. Diagram of cascade fractionating molecular still.

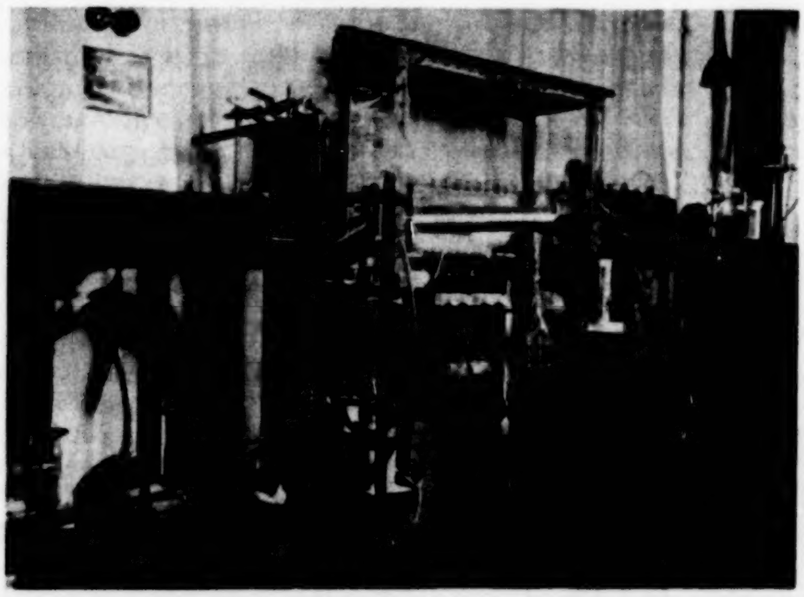

Fig. 2. Cascade fractionating molecular distillation equipment.

azelate in a similar apparatus. The plate number was determined by the McCabe-Thiele graphical procedure because the deviation from constant relative volatility was too great to permit the algebraic method of Fenske. The equilibrium curve was drawn according to data from WILLIAMS[3] who determined the vapour-liquid equilibrium of this system at 1 mm Hg.

The results are summarized in Table I.

TABLE I

DISTILLATION OF MIXTURES OF DI-*n*-BUTYL PHTHALATE AND DI-*n*-BUTYL AZELATE

Temp.: 68° C; pressure: $<10^{-4}$ mm Hg; total reflux.

Still composition mole % phthalate	*Distillate composition mole % phthalate*	*Plate number*
19.5	80.0	12
32.2	78.1	9

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The degree of separation attained in the molecular still is thus the same as can be achieved by distilling this particular mixture at 1 mm pressure using a column of 9 to 12 theoretical plates.

As we were mainly concerned with the problem of separating unreacted methyl esters of fatty acids from addition compounds with styrene, a trial distillation of a mixture of two model-compounds was performed. Methyl oleate and benzyl oleate were chosen for the following reasons:

(a) both compounds are liquid at room temperature,
(b) both compounds are distillable molecularly at favourable temperatures,
(c) the great difference in refractive index permits an easy and accurate analysis of binary mixtures,
(d) interesterification during distillation is not possible, both compounds being esters from the same acid.

Methyl oleate was prepared by esterification of oleic acid with excess methanol, using sulfuric acid as a catalyst. The ester was fractionated and the fraction 146.0-147.5° C/0.5 mm Hg was used. Its constants were: n_D^{20}: 1.4520; d_4^{20}: 0.8731; r_D^{20} (specific refraction according to Lorentz-Lorenz): 0.3090.

Benzyl oleate was prepared by esterification of oleic acid with benzyl alcohol in boiling xylene with sulfuric acid as a catalyst. The water formed during the reaction was removed continuously. The ester was fractionated and the fraction 199.5-200.5° C/0.5 mm Hg was used. Its constants were: n_D^{20} : 1.4969; d_4^{20}: 0.9386; r_D^{20}: 0.3117.

The refractive index determined for mixtures of varying composition is given in Table II.

TABLE II

MIXTURES OF METHYL OLEATE AND BENZYL OLEATE

mole % methyl oleate	n_D^{20}
100.0	1.4520
91.5	1.4567
77.9	1.4636
66.2	1.4692
55.6	1.4744
37.2	1.4825
13.7	1.4918
0.0	1.4969

The results of the distillation are summarized in Table III and are shown graphically in Fig. 3.

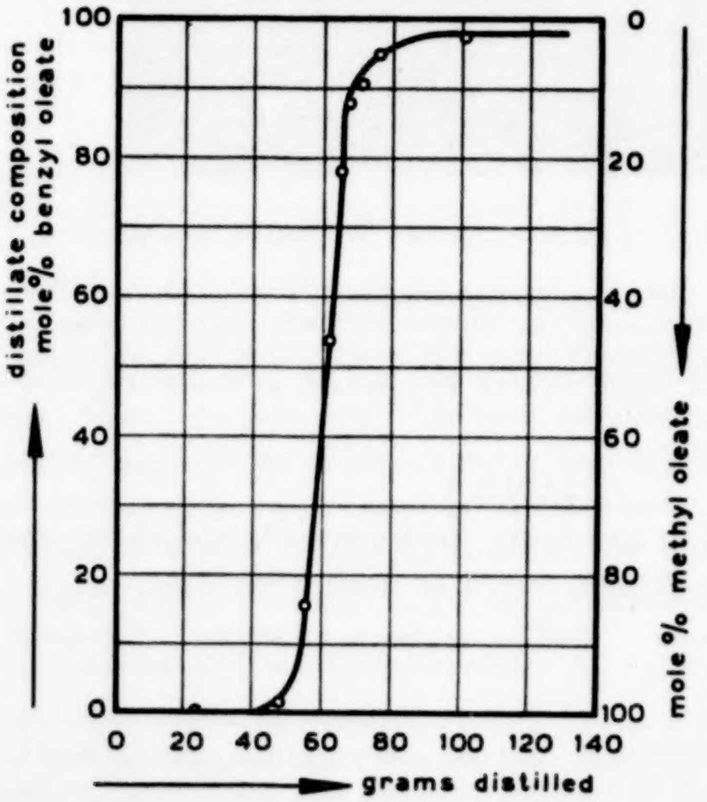

Fig. 3. Distillation curve of a methyl oleate-benzyl oleate mixture.

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As will be seen, the distillation curve is of the same type as encountered in ordinary batch distillations. A good separation has been achieved as methyl oleate of at least 99% purity and benzyl oleate of 97.5% purity could be isolated.

TABLE III

DISTILLATION OF A METHYL OLEATE — BENZYL OLEATE MIXTURE

Still charge: 126.6 g. Temp.: 85-135° C (measured at the outside of the heating surface). Pressure: $5 \cdot 10^{-4}$ mm Hg. Reflux ratio: 7.5: 1. Take-off rate: 15 ml/h

Grams distilled	n_D^{24}	*Mole % methyl oleate in distillate*
23.3	1.4520	100.0
48.0	1.4531	98.5
54.8	1.4604	84.5
61.9	1.4786	46.0
65.2	1.4888	22.0
67.2	1.4925	12.0
71.4	1.4934	9.5
75.9	1.4950	5.0
101.3	1.4960	2.5

Styrenization of methyl esters of linseed oil fatty acids

The mixed esters of linseed oil, prepared by saponification of linseed oil and esterification of the fatty acids with excess methanol (using sulfuric acid as a catalyst) were distilled at 150-161° C/0.5 mm Hg to yield a colourless product having the following constants: n_D^{20}: 1.4633; d_4^{20}: 0.8892; r_D^{20}: 0.3100; saponification value: 194.1 iodine value (Wijs' method): 183.

The styrenization was carried out with gaseous styrene in a glass column packed with Raschig rings according to BOELHOUWER, TJOA SOE TJOAN AND WATERMAN[4]. 170 ml esters were styrenated batchwise under the following conditions:

Temperature of column, styrene inlet and nitrogen inlet: 280° C
Styrene addition rate: 40 g/h Nitrogen rate: 1.5 l/h
Reaction time: 5½ h.

Before and after the addition of styrene the esters were kept at 280° C for 20 minutes while 6 l/h of nitrogen were passed through the product to remove volatile matter.

After cooling to room temperature in an atmosphere of nitrogen the clear, light yellow product had the following constants: n_D^{20}: 1.5110; d_4^{20}: 0.9680; r_D^{20}: 0.3095; S.V.: 135.4; Wt. % styrene (calculated from sap. value): 30.3.

Molecular distillation of styrenated esters

The results of the distillation are summarized in Table IV.

As the static holdup of the still was considerable (due to the high viscosity) this material was recovered by refluxing benzene in the still at atmospheric pressure several times. The benzene was removed by distillation; the product was freed from last traces of solvent under vacuum at 150° C.

The distillation losses amounted to 1.9 g (1.2% of still charge). The total styrene content of the fractions is 47.5 g while 48.2 g styrene was originally present.

All products were clear oils with gradually increasing viscosity.

DISCUSSION OF THE RESULTS

Contrary to the distillation of PETIT AND FOURNIER no cracking of the products was observed, thus the styrene content may be calculated from the saponification values. The reliability of this method is illustrated by the good agreement between total styrene content before and after distillation.

From Table IV it will be seen that a striking parallelism exists between refractive index, density, saponification value, styrene content, equivalent weight and colour. This is also brought out graphically for the refractive index and saponification value

TABLE IV

DISTILLATION OF STYRENATED ESTERS

Still charge: 159.0 g. Pressure: $1\text{-}5 \cdot 10^{-4}$ mm Hg. Reflux ratio: 7.5:1. Take-off rate: 15 ml/h at the beginning, 2 ml/h at the end of the distillation.

Fraction no.	*Weight g*	*Temp. °C a)*	*Colour b)*	n_D^{20}	d_4^{20}	r_D^{20}	*S.V.*	*Wt% styrene c)*	*Mole styrene per mole ester*	*Equivalent weight*	*Average mol. weight d)*	*Weight of styrene in fraction g*
1	1.27	120	SY	1.4882	0.9211	0.3129	143.5	25.2	1.0	391	—	0.32
2	1.48	—	SY	1.4823	0.9121	0.3127	150.0	21.8	0.8	374	—	0.32
3	2.24	—	W	1.4678	0.8980	0.3095	180.0	6.2	0.2	312	—	0.14
4	5.41	—	W	1.4637	0.8928	0.3089	187.1	2.5	0.1	300	—	0.13
5	7.55	—	W	1.4622	0.8967	0.3067	191.5	0.2	0.0	293	295	0.01
6	6.67	—	W	1.4626	0.9003	0.3057	188.7	1.6	0.0	297	—	0.11
7	5.80	—	W	1.4726	0.9023	0.3107	176.3	8.1	0.2	318	—	0.47
8	6.23	—	SY	1.4948	0.9330	0.3124	141.4	26.3	1.0	397	320	1.64
9	4.91	157	SY	1.4943	0.9389	0.3103	144.0	24.9	0.9	390	—	1.22
10	4.87	—	W	1.4687	0.9039	0.3080	175.2	8.7	0.3	320	—	0.42
11	5.47	—	W	1.4633	0.8927	0.3087	188.6	1.7	0.0	298	298	0.09
12	4.51	—	W	1.4740	0.9162	0.3067	172.9	9.9	0.3	325	—	0.45
13	4.78	—	SY	1.4972	0.9448	0.3098	140.5	26.7	1.0	400	—	1.28
14	7.95	—	SY	1.5078	0.9589	0.3108	133.4	30.4	1.2	420	—	2.42
15	7.11	—	LY	1.5230	0.9839	0.3105	118.6	38.2	1.7	474	429	2.72
16	6.00	192	LY	1.5231	0.9841	0.3105	120.0	37.4	1.7	467	—	2.24
17	3.05	—	LY	1.5206	0.9802	0.3104	119.2	37.8	1.7	471	—	1.15
18	2.91	—	LY	1.5258	0.9910	0.3096	117.0	39.0	1.8	480	—	1.13
19	3.83	—	LY	1.5300	0.9982	0.3095	117.1	38.9	1.8	480	—	1.49
20	4.50	—	LY	1.5293	0.9989	0.3089	117.4	38.8	1.8	478	—	1.75
21	1.64	210	LY	1.5287	1.0090	0.3056	120.3	37.3	1.7	467	—	0.61
22	2.72	—	LY	1.5274	1.0031	0.3067	122.0	36.4	1.6	460	—	0.99
23	2.94	—	LY	1.5310	1.0086	0.3068	118.9	38.0	1.7	472	—	1.12
24	2.94	—	LY	1.5341	1.0095	0.3079	114.9	40.1	1.9	489	—	1.18
25	3.31	—	LY	1.5360	1.0148	0.3073	113.9	40.6	1.9	493	670	1.34
26	2.14	—	LY	1.5377	1.0182	0.3070	114.5	40.3	1.9	490	—	0.86
27	1.86	254	LY	1.5380	1.0207	0.3064	112.9	41.1	2.0	497		0.76
Residue	43.0	—	YB	1.5475	1.0328	0.3073	97.6	49.1	2.7	575	— —	21.1
Total	157.1											7.5

Notes:

a) measured at the outside of the heating surface.

b) SY = slightly yellow, almost white
W = water-white
LY = light yellow
YB = yellowish brown.

c) calculated from:

$$\text{wt. \% styrene} = \frac{191.8 - \text{S.V.}}{191.8}\ 100\%$$

191.8 being the theoretical sap. value for methyl linolenate.

d) ebullioscopically in benzene.

in Fig. 4. From the rather sharp breaks in the curve the conclusion may be drawn that a good separation has been achieved.

Fractions 4, 5, 6 and 11 clearly represent unstyrenated monomeric esters. The equivalent and molecular weights found agree closely with those calculated for methyl esters of C18 fatty acids (296.5, 294.5 and 292.5 for methyl oleate, linoleate and linolenate respectively). The specific refraction however, is lower than in the case of the original esters. This may be ascribed to a certain degree of isomerization.

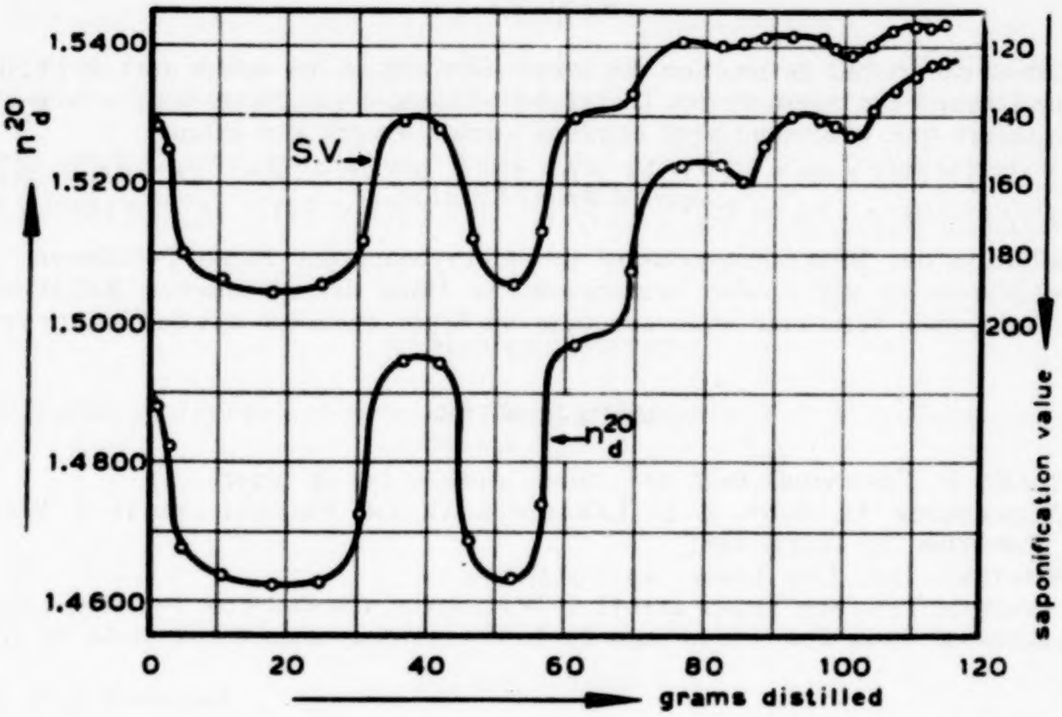

Fig. 4. Distillation of styrenated methyl esters of linseed oil fatty acids.

Though fractions 1, 2, 8 and 9 contain about one mole styrene per fatty acid chain, these products are not to be regarded as pure addition compounds of styrene and ester, since their molecular weights are obviously too low (calc. mol. wt. for monostyrenated ester: *ca.* 398). Therefore, it seems probable that these fractions contain low molecular weight polymers of styrene (dimer and trimer).

From fraction 13 on, all products contain considerable amounts of styrene. As their specific refractions are low notwithstanding the high styrene content (values of 0.3492 and 0.3499 have been reported[5] for the spec. refraction of monomeric styrene at 20° C), either the styrene must have polymerized to a very high degree or it must have combined chemically with the fatty acid esters. We may reject the first assumption as the products contain no products of very high molecular weight. Moreover, we calculated specific refractions for mixtures of completely dimerized esters (assuming dimerization by diene reaction) and polystyrene of infinite molecular weight and found that from fraction 15 on the experimental specific refractions are well below those calculated. We must conclude therefore, that we are dealing with compounds rather than mixtures of esters and styrene polymers.

No attempt was made to identify individual compounds. Instead, the reaction with styrene will be carried out with pure fatty acids as this will result in a less complex product.

ACKNOWLEDGEMENTS

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SUMMARY

The distillation of the reaction product of methyl esters of linseed oil fatty acids and gaseous styrene at 280° C in a highly efficient molecular still is described. From the specific refractions of the fractions obtained it follows that styrene has combined chemically with the esters.

RÉSUMÉ

La distillation du produit de réaction des esters méthyliques des acides gras de l'huile de lin et du styrène gazeux à 280° C est décrite. D'après les réfractions spécifiques des fractions obtenues, l'on peut conclure que le styrène s'est combiné chimiquement aux esters.

ZUSAMMENFASSUNG

Die Destillation des Reaktionsproduktes der Methylester der Leinöl-Fettsäuren, und des gasförmigen Styrols bei 280° C wird beschrieben. An Hand der spezifischen Refraktionen der erhaltenen Fraktionen kann man schliessen, dass das Styrol chemisch mit den Estern verbunden ist.

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THE USE OF OXINE IN THE ANALYSIS OF COMMERCIAL ALUMINIUM SULPHATE — A STATISTICAL APPROACH

by

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INTRODUCTION

It happens, all too often, that analyses directly following methods given in the literature give inaccurate results. Frequently, the method has been cursorily investigated, general conclusions being reached on very particular evidence or on inadequate data. On the other hand, the basis of the method is often good, and it is therefore only necessary to investigate factors (some of them by no means obvious) that have been neglected by the author. In cases where factors have been investigated, this has been done by varying them one at a time, a method which may be termed the "classical" approach. A more convenient, more revealing and less time consuming approach is that adopted in the present investigation. It is based on the familiar factorial experiment, examples of which have been given by BOX[1].

The above remarks can be applied to the determination of aluminium using oxine. For some time we have experienced difficulty in the accurate determination of aluminium and iron in commercial aluminium sulphate by precipitation as the hydroxides followed by ignition to oxides. It was therefore desired to replace this method by the widely advocated oxine method. When the latter was tried, however, following procedures recommended in the literature, low and often erratic results were obtained.

The commercial aluminium sulphate to be analysed contained about 9.1% aluminium and 0.35% of iron (both ferrous and ferric). The proportion of other metals did not exceed 0.1% mainly as manganese and magnesium with traces of titanium, and were found not to interfere in the determination. It was desired to precipitate aluminium and iron oxinates together and to determine iron on a separate portion of the sample. This was considered to be the simplest procedure, since, although methods for their separation and determination as oxinates have been suggested[2,3], a method for the analysis of iron which is more rapid than the gravimetric oxine method has been developed in our laboratories[4]. It will be appreciated that, provided the mixed oxinate determination is accurate, slight errors in the determination of iron would be unimportant, since the proportion of the latter is small. For this reason also, preliminary experiments were concerned with determinations of aluminium alone; the effect of the presence of iron was investigated later.

EXPERIMENTAL

In the preliminary experiments, **Moyer and Remington**'s procedure[3] for the precipitation of iron and aluminium oxinates together was tested and found to give erratic results. Slightly better, but low, results were obtained using **Kolthoff and Sandell**'s method[5], and further investigation was based on this simpler procedure. It involves the addition of oxine to an acidic aluminium solution, heating to about 60° C, and precipitation by the slow addition of an excess of $2N$ ammonium acetate.

A useful review on the determination of aluminium by oxine has appeared in a paper by **Miller and Chalmers**[6], who were primarily interested in a micro-method. According to these authors the factors of importance in the analysis are the rate of addition of ammonium acetate and the excess of oxine used. Too great a rate of addition of acetate caused significant positive errors, and when the acetate was added very slowly, with constant (magnetic) stirring, the precision was greatly improved. A major feature of **Miller and Chalmers**' experiments was a roughly linear relationship between the weight of excess oxine used and the percentage error in the weight of the precipitate.

Determinations following the principles of **Kolthoff and Sandell**[5] and the recommendations of **Miller and Chalmers**[6] were carried out. Aliquots of acidic solutions of aluminium made from 99.95 + % aluminium wire were used. Ammonium acetate was added dropwise while the solutions were stirred on a bank of magnetic stirrers capable of handling six beakers at a time. The glass-enclosed iron stirrers were weighed prior to the determination and, during filtration, were allowed to fall into the sintered glass crucibles with the precipitate. The results obtained were as follows:

Number of determinations:	12
Mean weight of precipitate:	0.4351 g (Theory 0.4367 g)
Standard deviation:	0.0006 g

While these results are consistent, they are low and it was therefore decided to design a factorial experiment to ascertain the relative importance of the sources of error. The experiment was constituted as described below, the factors considered being:

A) the volume of water used to dilute the aliquot of aluminium solution (V_{H_2O});
B) the volume of excess oxine solution used (V_{ox});
C) the temperature to which the solution was heated before precipitation (T_1°C);
D) the volume of excess ammonium acetate used (V_{ac});
E) the volume of solution used to wash the precipitates (V_{wash});
(A 1% ammonium acetate solution was used for washing, as it was considered that the precipitates would be less liable to peptization in ammonium acetate solution than in water).
F) the temperature of drying of the precipitates (T_2°C);
other factors were kept constant as will be apparent.

A weighed stirrer was inserted in a beaker, 20 ml of an acidic aluminium solution (1.5219 g Al/l) pipetted in, and this diluted with V_{H_2O} ml of water. The oxine was added in an excess of V_{ox} ml, and the solution was heated to T_1°C, determined with a thermometer. The magnetic stirrer was switched on, the thermometer rapidly rinsed with a small quantity of water, and $2N$ ammonium acetate run in at the rate of 2 ml/min until precipitation started, followed by a further V_{ac} ml at the same rate. Stirring was then stopped, the precipitate allowed to stand for 1-2 h and filtered off on a sintered glass crucible using a total of V_{wash} ml of 1% ammonium acetate

TABLE I FACTORI

	V_{H_2O} (ml)	25					
	V_{ox} (ml)	5.5				15	
	T_1 (°C)	40		60		40	
	V_{ac} (ml)	50	75	50	75	50	75
V_{wash}=200 ml	T_2 = 110° C	0.5254*	0.5264*	0.5265*	0.5210	0.5204	0.5202
	T_2 = 140° C	0.5199	0.5197	0.5175	0.5182	0.5197	0.5201
V_{wash}=300 ml	T_2 = 110° C	0.5223	0.5260*	0.5253*	0.5196	0.5194	0.5216
	T_2 = 140° C	0.5181	0.5173	0.5172	0.5177	0.5188	0.5199
		Weights of oxinat					

* These precipitates were left in a desiccator for an excessive time and formed a dark yellow cru

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solution. The precipitates were finally dried for 1 h at T_2°C, cooled for $\frac{1}{2}$ h in a desiccator, allowed to stand in the balance for 10 minutes and then weighed. The oven-drying and weighing were repeated until the weight was constant.

The results are shown in Table I, the theoretical weight of precipitate being 518.5 mg. As shown in the table, some of the results recorded are invalidated, because the precipitates were inadvertently left in a desiccator for an excessive time and formed a dark yellow crust on the surface. It will be noted that these results are unusually high.

A statistical analysis was carried out with the invalid results replaced by fictitious values to preserve the symmetry of the calculation. These fictitious values were computed in such a way as to leave the mean value of the observations (0.5193 g) unaltered and to keep the residual variance computed from all interaction terms at a minimum. The overall standard error of the observations, taking all sources of variation into account was estimated at 1.44 mg.

The effects of the main factors are given below. With one exception, there were no significant first order interactions. The 95% confidence range for any one effect was found to be ± 0.44 mg.

A) The volume of water used to dilute the aluminium solution did not effect the results.
B) A change in excess of 2% oxine from 5.5 ml to 15.5 ml resulted in a significant mean increase of 0.71 mg in the weight of the precipitate.
C) Increase in the temperature of the solution before precipitation from 40° to 60° C caused the weight of the precipitates to drop by 1.23 mg, a significant amount.
D) A change in the volume of $2N$ ammonium acetate from 50 to 75 ml did not affect the results. A 50 ml excess was therefore sufficient.
E) Increase in the volume of wash solution from 200 to 300 ml resulted in a significant mean decrease of 0.50 mg in the weight of precipitate obtained.
F) The temperature of drying was by far the most important factor, resulting in a decrease of 1.62 mg when the temperature was raised from 110° C to 140° C. It was not very practical, however, to dry at 110° C, since at this temperature the time required for the precipitate to attain constant weight was found to be excessive and the results obtained were high. In contrast, drying at 140° C was rapid and the mean of all results obtained at this temperature agreed almost exactly with the theoretical. Generally a temperature of 110° C is entirely adequate for drying a precipitate. In this case, however, it was found that there was a significant interaction between the excess of oxine used and the drying temperature, and it is possible that the process occurring in the oven was not a simple removal of excess water. This interaction was examined in a later factorial experiment.

In view of the element of doubt introduced by the faulty observations mentioned previously (all of which were from drying at 110° C) and because of the error involved in drying at 110° C, a statistical analysis was carried out on the results obtained from drying at 140° C only. The significant effects of the main factors are listed below, no first order interaction being found to be significant.

B) Increase in the excess of oxine from 5.5 to 15.5 ml resulted in a mean increase in the weight of precipitate of 1.49 mg.
C) Increase in the temperature of the solution before precipitation from 40° C to 60° C caused a mean decrease of 1.13 mg.

PERIMENT ON ALUMINIUM

		75							
		5·5				15·5			
60		40		60		40		60	
50	75	50	75	50	75	50	75	50	75
5206	0.5207	0.5212	0.5231	0.5185	0.5191	0.5213	0.5206	0.5184	0.5187
5185	0.5185	0.5180	0.5187	0.5169	0.5158	0.5209	0.5198	0.5195	0.5194
5202	0.5184	0.5211	0.5197	0.5187	0.5179	0.5212	0.5188	0.5207	0.5201
5181	0.5182	0.5176	0.5172	0.5169	0.5174	0.5198	0.5196	0.5188	0.5184
recipitate in g									

the surface.

E) Increase in the volume of solution used to wash the precipitates from 200 to 300 ml caused a mean decrease of 0.63 mg.

These conclusions are generally the same as were obtained when all the results were considered.

It should be mentioned that the increases and decreases in the weight of precipitate, caused by changes in the levels of the various factors, do not necessarily cancel each other out. The essential point of the factorial experiment was that it indicated which factors had to be controlled and how closely the control had to be effected.

In planning the second factorial experiment, designed primarily with a view to investigating the effect of iron and the interaction between the excess of oxine and the drying temperature, the levels of the non-significant factors already investigated were chosen arbitrarily. Thus the volume of water used to dilute the solution was 50 ml, the temperature of the solution before precipitation was 60° C, the excess of $2N$ ammonium acetate used was 50 ml and the volume of solution used to wash the precipitates was 250 ml.

The concentration of the aluminium solution used was 1.3283 g Al/l, and that of the iron 0.1000 g Fe/l. The experiment was carried out in the same way as the previous one, using 20 ml aliquots of aluminium solution and either 10 or 20 ml of iron solution. The theoretical weight of combined oxine precipitates was therefore either 0.4611 or 0.4698 g. To the solution of aluminium and iron was added 50 ml of water and 5 ml of 10% nitric acid and the solution was boiled for 1 minute (Such an oxidation with nitric acid would be necessary in the case of commercial aluminium sulphate and was found to be without effect on the determination). The solution was cooled to about 60° C, and the oxine added, the two levels of excess being again about 5.5 and 15.5 ml. The procedure was then the same as before except that the drying temperatures chosen were 120, 130 and 140° C.

If, as an approximation, a linear dependence of the weight of oxinate precipitate upon V_{ox}, T_1 and V_{wash} is assumed, the above choice of $T_1 = 60°$ C and $V_{\text{wash}} = 250$ ml should give a mean precipitate weight in close agreement with the theoretical when the total volume of oxine is 37.5 ml ($V_{\text{ox}} = 15.5$ ml) but a low result when $V_{\text{ox}} = 5.5$ ml. This conclusion is based on the results of the first factorial experiment and is borne out by the determinations which are recorded in Table II. The weights of precipitates obtained with the higher excess of oxine are extremely satisfactory.

TABLE II

FACTORIAL EXPERIMENT ON THE DETERMINATION OF ALUMINIUM AND IRON TOGETHER

V_{Fe} ml	10						20					
V_{ox} ml	5.5			15.5			5.5			15.5		
T°C	120	130	140	120	130	140	120	130	140	120	130	140
	0.4602	0.4599	0.4595	0.4614	0.4612	0.4601	0.4682	0.4707	0.4671	0.4698	0.4714	0.4700
	0.4600	0.4601	0.4590	0.4615	0.4611	0.4614	0.4685	0.4710	0.4684	0.4699	0.4697	0.4699
	Mean = 0.4598 Theoretical = 0.4611			Mean = 0.4611 Theoretical = 0.4611			Mean = 0.4690 Theoretical = 0.4698			Mean = 0.4701 Theoretical = 0.4698		
	Weights of oxinate precipitate in g											

Statistical analysis showed that, as before, the excess of oxine had a profound effect on the weights of precipitate obtained. There was also a slight suggestion of an interaction between the excess of oxine and the temperature of drying, but not nearly as marked as in the first experiment. The analysis of variance suggested that the most suitable drying temperature would be 130° C, but drying took place a little more quickly at 140° C and this choice of temperature left the results correct; for further work therefore, 140° C was used.

Analysis of commercial aluminium sulphate; comparison of oxine method with other methods

In addition to the oxine method, two other methods were used for the analysis of commercial aluminium sulphate.

a) The direct ignition of the sample. For this about 2 g of aluminium sulphate were accurately weighed into a platinum crucible. After preliminary gentle heating, the samples were finally ignited to constant weight on a blast burner at about 1300° C. The aluminium content was obtained after subtracting the iron and insoluble matter present in the sample.

b) The "R_2O_3 method". This is the usual procedure involving double precipitation of the aluminium and iron as hydroxides, followed by ignition to mixed oxides at about 1300° C. The sample is dissolved in dilute sulphuric acid and filtered before the determination.

For the oxine method the sample was also dissolved in dilute acid and filtered. Knowing the approximate composition of the sample, the optimum excess of oxine as determined in the factorial experiments was used. Other conditions of analysis were also based on the factorial experiments.

Four samples, A, B, C, D, of aluminium sulphate, with different iron contents, were used. Each sample was carefully crushed, mixed and divided into 24 portions,

TABLE III

ANALYSIS OF COMMERCIAL ALUMINIUM SULPHATE — COMPARISON OF METHODS

Method	*Operator*	% Al_2O_3			
		Sample A (0.48% Fe_2O_3)	*Sample B* (0.54% Fe_2O_3)	*Sample C* (0.52% Fe_2O_3)	*Sample D* (0.50% Fe_2O_3)
1. Oxine	I	17.04 17.04	17.34 17.44	17.43 17.59	17.41 17.50
	II	16.95 17.07	17.30 17.45	17.54 17.58	17.40 17.30
	III	17.10 17.15	17.36 17.44	17.57 17.62	17.43 17.35
	IV	17.11 17.08	17.41 17.40	17.54 17.54	17.36 17.33
2. R_2O_3	V	17.25 17.23	17.47 17.61	17.63 17.72	17.57 17.60
Precipitation and ignition	VI	17.21 17.07	17.86 17.39	17.68 17.54	17.42 17.33
	VII	17.27 17.26	17.46 17.41	17.75 17.72	17.54 17.54
	VIII	16.52 17.77	17.24 17.69	17.41 17.23	17.09 17.70
3. Direct ignition	IX	17.15 17.13	17.47 17.50	17.68 17.63	17.49 17.50
	X	17.38 17.34	17.54 17.52	17.87 17.95	17.50 17.43
	XI	17.24 16.96	17.63 17.57	17.85 17.75	17.60 17.40
	XII	16.93 17.25	17.76 17.68	17.87 17.74	17.63 17.55

giving 96 portions in all. Each of the three methods was carried out in duplicate by four different operators, none of whom knew that any of the portions were the same. The order of the experiments was random. None of the operators was experienced in the direct ignition method. Of the four operators each carrying out the oxine and R_2O_3 methods, two were inexperienced (operators III and IV in the oxine method, and VII and VIII in the R_2O_3 method). Details of the results of the experiment are given in Table III.

The overall variation of the R_2O_3 method was considerably increased by the very discrepant observations of operator VIII. Although this fact itself is a citricism of the method, which fails all too easily in the hands of an inexperienced operator, the results of operator VIII were omitted in the statistical analysis, which led to the following conclusions:

1. The scatter of the results obtained by the R_2O_3 and ignition methods can be expected (with 95% confidence) to be between 1.4 and 2.8 times as great as that of the results by the oxine method.

$$\left(\frac{\text{Residual variance for } R_2O_3 \text{ method}}{\text{Residual variance for oxine method}} \sim \frac{\text{Residual variance for ignition method}}{\text{Residual variance for oxine method}} \sim 4\right)$$

2. The mean values (% Al_2O_3), their 95% confidence ranges and mean differences between results by the various methods are as follows:

Sample	Oxine Method (4 operators)	R_2O_3 Method (3 operators)	Ignition Method (4 operators)	Mean Differences 2-1	 3-1
A	17.07 ± 0.04	17.22 ± 0.10	17.17 ± 0.09	0.15	0.10
B	17.39 ± 0.04	17.53 ± 0.10	17.58 ± 0.09	0.14	0.19
C	17.55 ± 0.04	17.67 ± 0.10	17.79 ± 0.09	0.12	0.24
D	17.39 ± 0.04	17.50 ± 0.10	17.51 ± 0.09	0.11	0.12

The least significant difference (95% confidence) between an R_2O_3 and an oxine determination was found to be 0.11, and that between an ignition and an oxine determination 0.095. The above mean differences are therefore all significant.

3. The 95% confidence ranges for a single observation by the three methods are: Oxine ± 0.112; R_2O_3 ± 0.242; Ignition ± 0.240.

DISCUSSION

The consistent and accurate results obtained by the oxine method in the second factorial experiment and in the analyses of aluminium sulphate can generally be attributed to a rigid adherence to the chosen experimental conditions. It was considered that one of the important factors, and a probable main cause of erratic results obtained in the preliminary experiments, was the method of stirring. While consistent results may sometimes be obtained with hand stirring, there would always be an element of doubt attached to the procedure. The usual mechanical stirring was rejected because the precipitate adheres to the stirrer and its removal is often difficult.

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The difference in the consistency between the results obtained with the oxine method on the one hand and those of the R_2O_3 and ignition methods on the other is striking. The reason for the discrepancy was not, however, investigated. The R_2O_3 method is comparatively tedious and the errors have been discussed at length in the literature[7]. While the direct ignition method is rapid, it also has the disadvantage associated with ignitions of alumina, and probably has other sources of error as well.

RECOMMENDED PROCEDURE

For analyses of aluminium or aluminium and iron in solutions containing the equivalent of about 30 mg of aluminium per determination, the following procedure will give good results:

Pipette a suitable aliquot of the solution into a beaker containing a weighed magnetic stirrer bar. If required, oxidize the iron by boiling with 5 ml of 10% nitric acid. Cool to about 40° C, add a 15.5 ml excess of 2% oxine in N acetic acid solution and heat to 63° C. Place the beaker on the magnetic stirrer and switch this on. When the temperature has dropped to 60° C, add $2N$ ammonium acetate at the rate of 2 ml/min until precipitation starts and then a further 50 ml at the same rate. Allow the precipitate to stand for about 1 h and filter through a number 4 porosity sintered glass crucible, carefully allowing the stirrer to enter the crucible with the precipitate. Use a total of 250 ml of 1% ammonium acetate for both removing the precipitate from the beaker and washing it on the crucible. Do not allow the crucible to suck dry until filtration is complete. Dry the precipitate at 140° C, cool in a desiccator for ½ h, place in the balance case for 10 min and weigh. Repeat to constant weight.

ACKNOWLEDGEMENTS

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SUMMARY

The analysis of commercial aluminium sulphate by precipitation of the aluminium and iron with 8-hydroxyquinoline (oxine) has been investigated. Factorial experiments were used to determine what control of experimental conditions was required for accurate results. The oxine method was compared with other methods and found to be considerably more accurate and precise, provided that correct conditions of precipitation were rigidly adhered to.

RÉSUMÉ

L'analyse du sulfate d'aluminium par précipitation de l'aluminium et du fer au moyen de la 8-hydroxyquinoléine (oxine) a été examinée. Des essais factoriels ont été effectués pour déterminer les conditions expérimentales permettant d'obtenir des résultats exacts. Après comparaison avec d'autres méthodes, on arrive à la conclusion que l'analyse au moyen de l'oxine est la plus exacte et la plus précise, si l'on suit rigoureusement les conditions données pour la précipitation.

ZUSAMMENFASSUNG

Die Analyse von technischem Aluminiumsulfat wurde durch Fällung von Aluminium und Eisen mit 8-Hydroxychinolin (Oxin) ausgeführt. Durch faktorielle Experimente wurde festgestellt, welche Versuchsbedingungen genau beachtet werden müssen, um richtige Ergebnisse zu erlangen.

Die Oxin-Methode wurde mit anderen Methoden verglichen und als wesentlich genauer und richtiger als diese befunden — immer vorausgesetzt, dass die Fällungsbedingungen richtig eingehalten werden.

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CONTRIBUTION À L'ÉTUDE DE LA SÉPARATION DES TERRES RARES DE FISSION PAR L'ACIDE ÉTHYLÈNEDIAMINETÉTRAACÉTIQUE

par

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Les très grandes différences dans la stabilité des complexes des terres rares avec l'acide éthylènediaminetétraacétique, ont amené les chercheurs à étudier, depuis quelque temps, la séparation de ces terres rares en présence de ce complexant sur résine cationique.

A côté de chercheurs qui se sont attachés à étudier la séparation de terres rares dans un but de chimie préparative, MAYER ET FREILING[1], notamment, ont déterminé les conditions de séparation des mélanges Y-Tb-Eu-Sm pour des quantités de l'ordre de quelques mg: ils ont conclu à l'efficience particulière de l'EDTA par rapport aux autres complexants.

Le Laboratoire de Radiochimie de l'Université de Liège étudie, depuis bientôt 2 ans, l'utilisation de l'EDTA pour la séparation chromatographique des produits de fission de l'uranium**, et, en particulier, la séparation de terres rares.

Voici quelques résultats obtenus dans la séparation des éléments de longue vie; les terres rares employées sont d'abord séparées chimiquement des autres produits de fission selon le procédé décrit dans CORYELL ET SUGARMANN[2].

1. Séparation ^{61}Y-^{147}Pm-^{144}Ce (4 mg Y_2O_3 – Pm carrier free – Ce^{+3}: max. 20 γ de CeO_2. Mélange radioactif versé sur la résine à pH = 2.2).
   La Figure 1 montre une séparation déjà excellente à pH = 3.65 (mesuré à 80° C, température de la colonne). A pH = 3.05-3.1, (Fig. 2), la séparation est quantitative; la traînée qui suit le pic de l'yttrium paraît être due à un mélange Y-^{155}Eu, ainsi que semblent le montrer des décroissances suivies pendant quelques mois.

2. Pour résoudre ce problème, des mélanges synthétiques ^{61}Y-^{152}Eu ont été réalisés et des séparations entreprises (2 mg Y_2O_3-60 γ Eu_2O_3-versés à pH = 2.2 sur la résine).
   Ainsi que le montrent les Figures 3 et 4, la séparation, quasi nulle à pH = 3.5, devient presque quantitative à pH = 3.05-3.1. La traînée de la Figure 2 qui n'est observée que lorsqu'on descend à pH 3.1 paraît donc être due à l'^{155}Eu, très malaisé à mettre en évidence dans les produits de fission à cause de sa très faible teneur (0.02 à 0.03%) et de son rayonnement très peu pénétrant. Il est à noter comme argument supplémentaire que cette traînée s'observe au même endroit dans la séparation ^{61}Y-^{152}Eu à pH = 3.05.

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* Chercheur agréé à l'Institut Interuniversitaire des Sciences Nucléaires.

** Il nous est agréable de remercier M. HUBERT, Directeur au CEAEN qui a bien voulu mettre à notre disposition de l'U irradié ainsi que les radioisotopes nécessaires à cette recherche.

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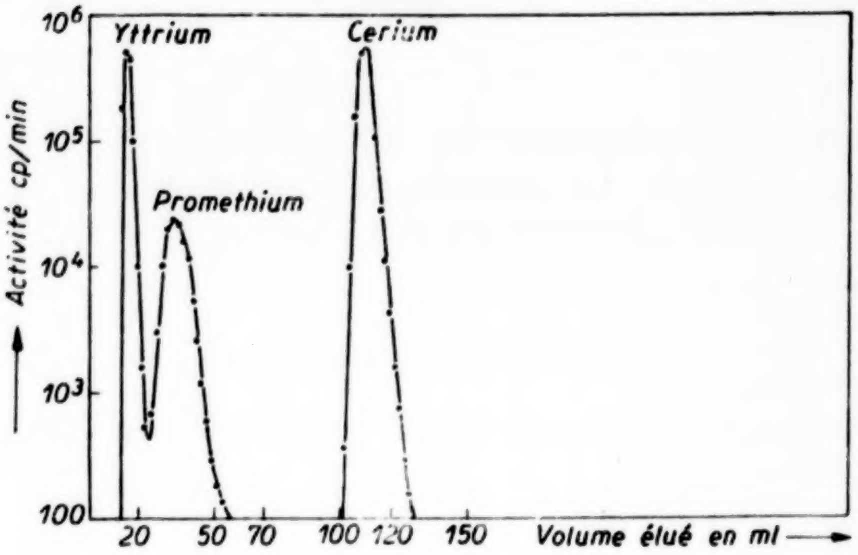

Fig. 1.

Dowex 50: 74-36 μ
Complexon II: $2.5 \cdot 10^{-2} M$
pH: 3.65 ± 0.05
T: 80° C
Résine NH_4: 12 g 53

Hauteur de colonne: 34.6 cm
Section: 1 cm^2
Volume libre: 12.15 ml
Vitesse d'élution: 0.88 $ml/cm^2/min$

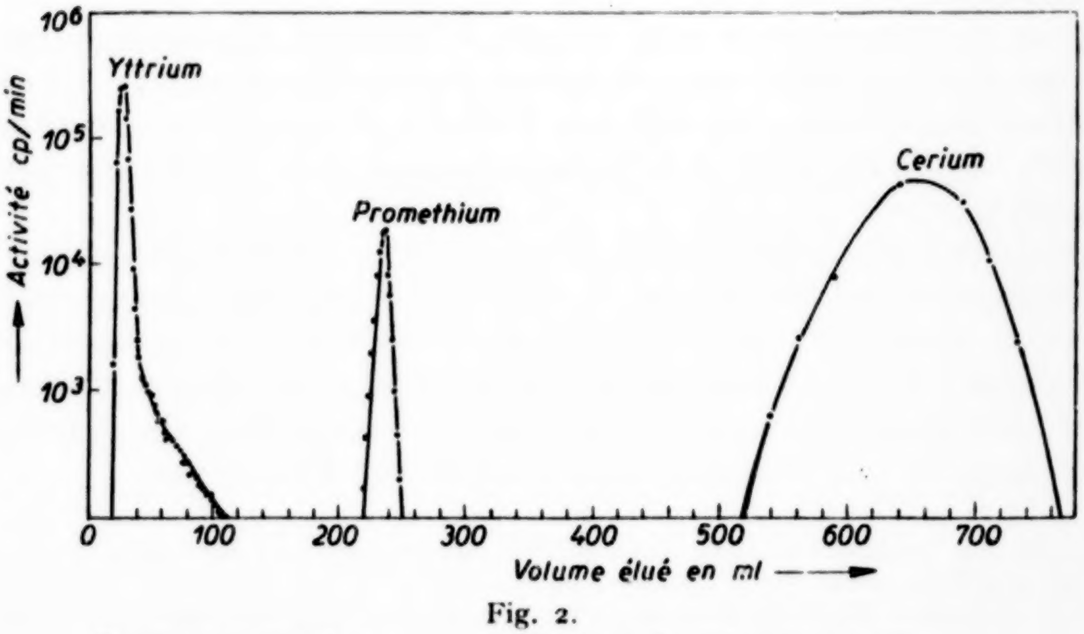

Fig. 2.

Dowex 50: 74-36 μ
Complexon II: $2.5 \cdot 10^{-2} M$
pH: 3.05-3.1
T: 80° C
Résine NH_4: 12 g 49

Hauteur de colonne: 35 cm
Section: 1 cm^2
Volume libre: 12.60 ml
Vitesse d'élution: 0.94 $ml/cm^2/min$

3. Cependant, les séparations à pH = 3.05 avec le complexon $2.5 \cdot 10^{-2} M$ sont malaisées; car la solution éluante est sursaturée à froid et elle finit par cristalliser au sortir de la colonne lorsque l'opération se prolonge. Une élution du mélange ^{61}Y-^{152}Eu-^{147}Pm-^{144}Ce à pH = 3.15-3.2, toutes autres conditions égales, ne présente pas ces inconvénients mais la séparation est beaucoup moins bonne ainsi que le montre la Figure 5.
Il est à remarquer, cependant, que dans cette séparation, les 2 pics-Y et Eu sont très raides et qu'entre eux, on constate un facteur de décontamination supérieur à 10, c'est-à-dire que les points maxima présentent une très grande pureté.

4. Une séparation Y-Eu-Pm-Ce a été de nouveau réalisée, directement cette fois sur le mélange de fission et dans des conditions expérimentales meilleures que celles de la séparation indiquée par la Figure 2. Dans cette séparation, on constate effectivement la présence du pic de l'^{155}Eu,

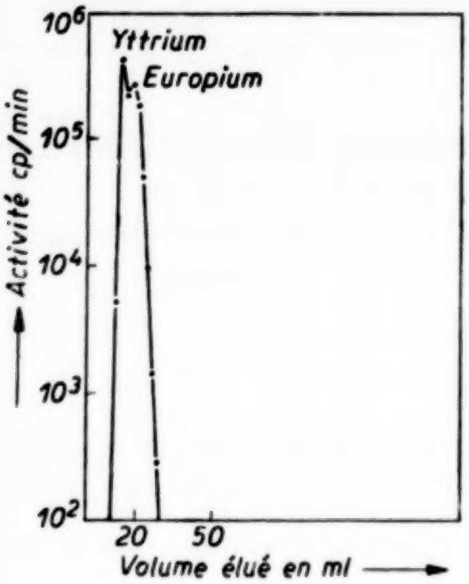

Fig. 3.

Dowex 50: 74-36 μ
Complexon II: $2.5 \cdot 10^{-2} M$
pH: 3.5
T: 80° C
Résine NH_4: 12 g 49
Hauteur de colonne: 33.4 cm
Section: 1 cm²
Volume libre: 12.00 ml
Vitesse d'élution: 0.80 ml/cm²/min

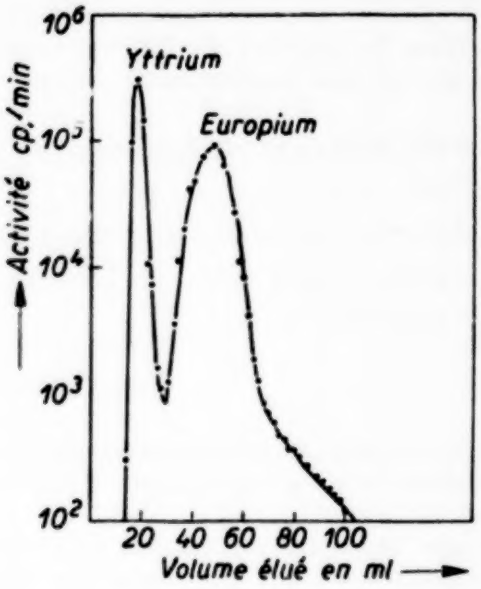

Fig. 4.

Dowex 50: 74-36 μ
Complexon II: $2.5 \cdot 10^{-2} M$
pH: 3.05-3.1
T: 80° C
Résine NH_4: 12 g 49
Hauteur de colonne: 33.4 cm
Section: 1 cm²
Volume libre: 12.00 ml
Vitesse d'élution: 0.81 ml/cm²/min

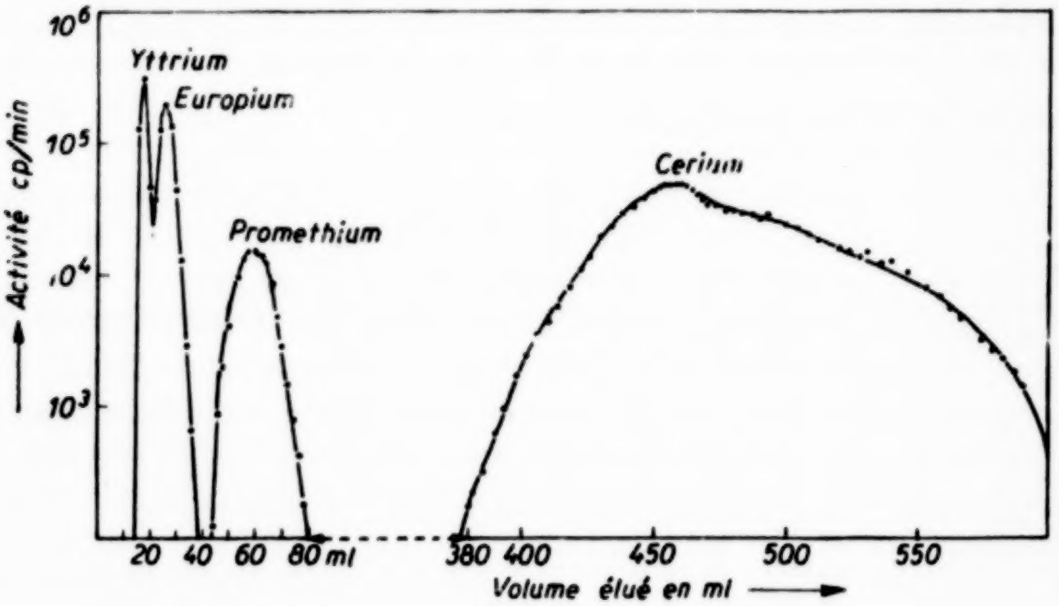

Fig. 5.

Dowex 50: 74-36 μ
Complexon II: $2.5 \cdot 10^{-2} M$
pH: 3.15-3.2
T: 80° C
Résine NH_4: 12 g

Hauteur de colonne: 33.4-.5 cm
Section: 1 cm²
Volume libre: 12.2 ml
Vitesse d'élution: 0.59 ml/cm²/min

très petit (le max. du pic est à 750 c/') alors que celui de l'Y, dans cette séparation, est à 130.000 c/') mais bien séparé. Des mesures d'absorption du rayonnement dans l'Al montrent qu'il s'agit bien de ^{155}Eu. La certitude sera absolue, lorsque, pendant quelques mois encore, nous aurons suivi la décroissance de cet élément.

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En conclusion, toutes autres conditions inchangées, nous proposons de travailler à pH = 3.05 pour éluer Y-Eu-Pm puis d'élever le pH à 3.65. Cette façon d'opérer permet de recueillir le Ce dans un volume relativement réduit.

La recherche est actuellement poursuivie moyennant diverses modifications techniques.

Il nous est agréable de remercier MM. Gueben et Govaerts pour leur précieuse collaboration, ainsi que le Directeur de l' I. I. S. N. pour les subsides qui nous ont été accordés.

RÉSUMÉ

Dans le présent article, les auteurs recherchent les conditions d'une séparation rapide et si possible analytique d'un mélange Y-Eu-Pm-Ce pour des quantités de l'ordre de quelques milligrammes.

On donne des courbes d'élution en fonction du pH, qui est le facteur d'influence prépondérant. Une séparation à pH 3.05 donne les meilleurs résultats.

SUMMARY

In the present paper, the authors investigate the conditions for a rapid and if possible analytical separation of a mixture Y-Eu-Pm-Ce for quantities of a few milligrams.

Elution curves are given in function of the pH, which is the main influencing factor.

A separation at pH 3.05 gives the best results.

ZUSAMMENFASSUNG

In diesem Artikel, untersuchen die Autoren die Bedingungen einer raschen und wenn möglich analytischen Trennung einer Mischung von Y-Eu-Pm-Ce für Mengen von wenigen Milligrammen.

Elutionskurven in Abhängigheit vom pH, welcher der überwiegende Einflussfaktor ist, werden gegeben.

Eine Trennung bei pH 3.05 gibt die besten Ergebnisse.

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THE DIETHYLDITHIOCARBAMATE OF MERCURY: COMPOSITION, STRUCTURE AND ANALYTICAL APPLICATION.

A HETEROMETRIC STUDY

by

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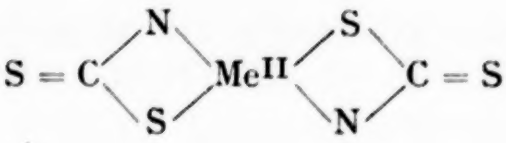
INTRODUCTION

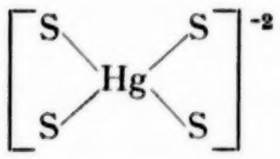
Our aim was to study the structure and composition of sulfides by the heterometric method (= photometric study of suspensions). It appeared to us that the heterometric method was most suited to this purpose. The use of alkaline sulfide solutions was excluded because they are not sufficiently stable. As compared to the latter, the sodium salt of diethyldithiocarbamate is soluble in water and the solution obtained is stable for a long time even at a 0.001*M* concentration. Mercuric carbamate was chosen for our investigation. It is insoluble in water and is colourless. It was found that the most insoluble mercuric compound which was obtained at room temperature, had the composition $Hg(CBM)_2$ (CBM = diethyldithiocarbamic anion). This compound could be obtained in acetic acid, acetate or ammoniacal solutions, in two ways: either by the heterometric titration of mercuric nitrate with Na(CBM) or vice versa. In addition to $Hg(CBM)_2$, intermediate compounds also exist, but they are quantitatively transformed into $Hg(CBM)_2$. The latter proved to be insoluble in the presence of most complexing agents. Pyro- and tripolyphosphate were without influence. Neither was the compound changed in citrate or ethylendiaminetetraacetic acid solutions containing large excesses of ammonia. Our experiments showed that $Hg(CBM)_2$ is the most insoluble of the carbamates of the bivalent cations.

Very many publications have appeared recently dealing with the analytical use of carbamates, especially for the determination of copper as well as of cadmium, zinc, *etc*. The compounds of mercury seem to be neglected. (The literature on carbamates can be taken from recent analytical handbooks.) The different carbamates are soluble in organic solvents as CCl_4, $CHCl_3$ and, in the case of coloured solutions, the latter are used for the quantitative photometric determination of metals at chosen wavelengths. All workers in this field have assumed that the metal carbamates obtained are *complex* compounds. Their structures have probably not been investigated although their compositions are cited as $Me^{II}(CBM)_2$, whilst those of the trivalent cations probably have the composition $Me^{III}(CBM)_3$.

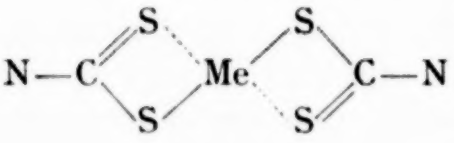
Difficulties are encountered in attempting to conceive the structure for $Me^{II}(CBM)_2$. Sterically, a structure such as:



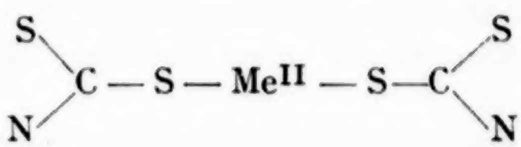
in which both the nitrogen and the sulfur, which are bound to the metal, come from the *same* carbamate, is extremely difficult to conceive. On the other hand, we know from our investigations, that ethylendiaminetetraacetate solutions containing large excesses of NH_3 have no influence on the $Hg(CBM)_2$ compound. The problem is therefore, firstly, how to present a general structure for the carbamates recognizing that they are very stable covalent compounds, and secondly, to establish if and when nitrogen is involved in the structure of $Me^{II}(CBM)_2$. In a previous report[1] we showed that a soluble anion complex with mercaptobenzthiazole is formed which has a structure:



With many cations CBM gives insoluble, frequently colourless, carbamates. Some amongst them have no affinity to nitrogen. It seems reasonable therefore not to include the nitrogen in the complex formation. On the other hand, if the structure is assumed to be



the same difficulties are encountered sterically.
It may well be that the formation of



is already sufficient to give a covalent compound. If four sulfurs participate in the compound, then they must come from four carbamate anions, and the $Me^{II}(CBM)_2$ would then have to be a dimer $(Me^{II}(CBM)_2)_2$ in the most simple case. On the other hand, the affinity of mercury to nitrogen may produce bonds of another character.

On studying the heterometric curves it can be seen that traces of either mercuric mercury or of CBM may be determined heterometrically with an error which is close to zero.

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EXPERIMENTAL

The heterometric method, which was developed by the first author and has already been discussed elsewhere[2,3] was used for this study. The curves obtained were used for the determination of mercury or CBM. All titrations were carried out at 20° C. 20 ml solution was used for the titration which was carried out in a vessel with a diameter of 4 cm. All reagents used were either analytical reagents or chemically pure reagents. A few drops of nitric acid were added to the concentrated stock solution of mercuric nitrate (mercuric nitrate crystallized reagent $Hg(NO_3)_2.H_2O$, Baker and Adamson). The more dilute solutions were then obtained by diluting in water. The sodium diethyldithiocarbamate was an Eastman pure product. The solutions of NaCBM were obtained by weighing the calculated amount of the salt which was then dissolved in water.

RESULTS AND DISCUSSION

pH — Heterometric titrations

A parallel pH and heterometric titration was carried out with 20 ml solution, which had the following composition:

3 ml $0.002M$ $Hg(NO_3)_2$ + 4 ml $0.025M$ Na_2H_2-ethylenediaminetetraacetate + 2 ml $0.007M$ sodiumdiethyldithiocarbamate + 3 ml H_2O + 2 ml $0.1N$ HNO_3 + 2 ml $0.1M$ CH_3COOH + 4 ml $0.1M$ NH_4NO_3.

The solution was titrated dropwise with $0.2M$ NaOH. At pH ∾ 2.5 a precipitate of mercuric carbamate alreadyappeared, and the density caused by the precipitate did not change until pH ∾ 11.5. A horizontal density line was obtained, showing that the precipitate is not influenced by the ethylenediaminetetraacetate whatever the pH conditions.

Titrations of mercury with CBM. Fig. 1 presents the composition and the results of titrations of an aqueous mercuric nitrate solution with Na(CBM). The concentration of mercury was between $0.75 \cdot 10^{-4}M$ and $3 \cdot 10^{-4}M$ (= 0.3012 mg Hg/20 ml — 1.2036 mg Hg/20 ml). The titrations were carried out in acetic acid, acetate or ammoniacal solution. In all cases at the end of the titration, straight maximum optical density lines were obtained and the maximum density *values* rose with the increased amount of mercury added.

In each case the *first* maximum optical density point (which indicates the end of the reaction) was obtained exactly at the molar ratio of 1 Hg : 2 CBM. The error was 0-2%. This means that a few tenths of a milligram of mercury in 20 ml aqueous solution or *one part of mercury in about* 50.000 *parts of water* can be determined by heterometric titration with CBM, with an error which is generally close to zero. The time was 15-30 minutes.

The curves obtained are rather interesting as the existence of additional mercuric-CBM compounds could be deduced from them. Thus, analysing curve 1 it may be established that the point of the initial precipitation lies at the molar ratio of 1 Hg : 1 CBM. Both above titrations were carried out in a dilute sodium acetate solution.

When the titration was carried out in acetic acid solution (curves 5 and 6), even at different concentrations of mercury, the point of the initial precipitation in both curves is at the same molar ratio, *i.e.* (1 Hg : 1 CBM ?). Curve 3, which was obtained when the titration was carried out in concentrated ammonia solution is more complicated. The last break lies at 1 Hg : 2 CBM but, in addition, another break is discernible.

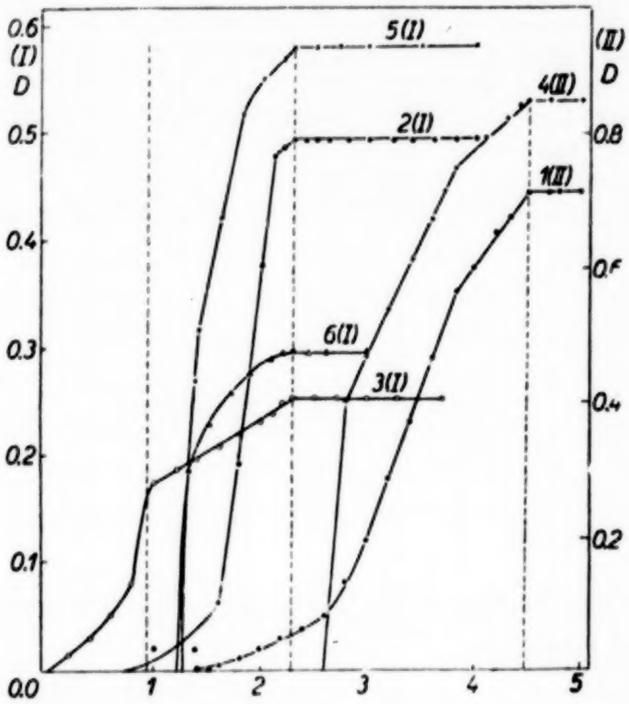

Fig. 1.

1) 3 $Hg(NO_3)_2$ 0.002*M* + 2 CH_3COONa 0.1*M* + 15 H_2O + x D.D.C.A. 0.0028*M*. Titration time 15 min.
2) 3 $Hg(NO_3)_2$ 0.001*M* + 2 CH_3COONa 0.1*M* + 15 H_2O + x D.D.C.A. 0.0028*M*. Titration time 55 min.
3) 3 $Hg(NO_3)_2$ 0.001*M* + 2 NH_3 2*M* + 15 H_2O + x D.D.C.A. 0.0028*M*. Titration time 25 min.
4) 3 $Hg(NO_3)_2$ 0.002*M* + 1 CH_3COOH *M* + 16 H_2O + x D.D.C.A. 0.0028*M*. Titration time 30 min.
5) 3 $Hg(NO_3)_2$ 0.001*M* + 1 CH_3COOH *M* + 16 H_2O + x D.D.C.A. 0.0028*M*. Titration time 15 min.
6) 3 $Hg(NO_3)_2$ 0.0005*M* + 1 CH_3COOH *M* + 16 H_2O + x D.D.C.A. 0.0014*M*. Titration time 20 min.

Titrations of sodium carbamate with mercuric nitrate. The results obtained in the reverse titration of CBM with mercury are compiled in Fig. 2. The final concentration of CBM was 0.0007*M* (curves 1 and 2) and 0.00033*M* (curves 3 and 4).

Analysing the curves, the following conclusions may be drawn. The maximum optical density values of experiments 1 and 2 are the same, but the character of the curves is different: in the ammoniacal solution (curve 2) excess of mercury causes no change, but in sodium acetate solution (curve 1) the excess of mercury gradually dissolves the precipitate. Probably, $Hg(CBM)_2$ is transformed into Hg(CBM) which is more soluble.

With lower concentrations of CBM the maximum density value in the presence of sodium acetate (curve 3) is much higher than with ammonia (curve 4). In both cases, horizontal maximum optical density lines were obtained. In all experiments, the first maximum optical density point lies at the end of the formation of $Hg(CBM)_2$. The error is practically equal to zero. 0.5-1.0 mg of Na(CBM) which was dissolved in 20 ml water were titrated with mercury and theoretical results were obtained. The titration time was about 40 minutes.

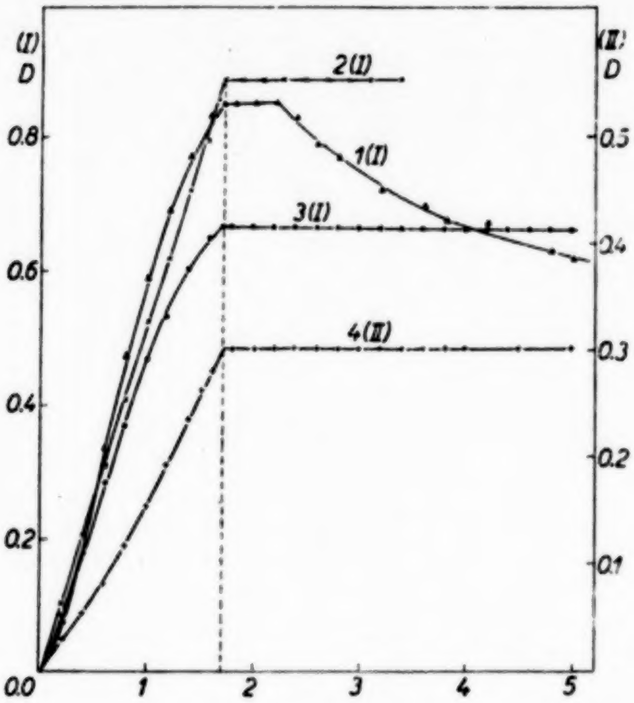

Fig. 2.

1) 5 D.D.C.A. 0.00 8M + 2 CH_3COONa 0.1M + 13 H_2O + x $Hg(NO_3)_2$ 0.004M.
Titration time 45 min.
2) 5 D.D.C.A. 0.0028M + 2 NH_3 2M + 13 H_2O + x $Hg(NO_3)_2$ 0.004M.
Titration time 45 min.
3) 5 D.D.C.A. 0.0014M + 2 CH_3COONa 0.1M + 13 H_2O + x $Hg(NO_3)_2$ 0.002M.
Titration time 40 min.
4) 5 D.D.C.A. 0.0014M + 2 NH_3 2M + 13 H_2O + x $Hg(NO_3)_2$ 0.002M.
Titration time 30 min.

CONCLUSIONS

Composition

1) Hg^{+2} when titrated heterometrically with sodium diethyldithiocarbamate (= Na(CBM)) in acetate or acetic acid solution, gives the first maximum density point exactly at the molar ratio of 1 Hg : 2 CBM.

Excesses of CBM have no influence on the compound obtained.

2) An intermediate, Hg(CBM), exists; it is more soluble than $Hg(CBM)_2$ and is transformed quantitatively into the latter compound.

3) The reverse titration of CBM with Hg^{+2}, giving the insoluble $Hg(CBM)_2$, can be carried out with the same success.

Analysis

0.3-1.2 mg Hg in 20 ml aqueous solution can be titrated with Na(CBM) 0.004M solution.

Or vice versa, 0.5-1.0 mg Na(CBM) in 20 ml aqueous solution can be titrated with mercuric nitrate, 0.002M-0.004M. The error in both cases is mostly equal to zero. Both titrations can be carried out in acidic, alkaline or ammoniacal solutions.

SUMMARY

0.3—1.2 mg of mercury (= $Hg(NO_3)_2$) in 20 ml aqueous solution, can be titrated heterometrically with sodium diethyldithiocarbamate (NaCBM).

Vice versa, 0.5—1.0 mg NaCBM in 20 ml aqueous solution can be titrated heterometrically with mercuric nitrate.

In both cases the error is mostly equal to zero. The insoluble $Hg(CBM)_2$ is obtained in both cases.

RÉSUMÉ

0.3—1.2 mg de mercure (= $Hg(NO_3)_2$) dans 20 ml de solution aqueuse peuvent être titrés hétérométriquement avec le diéthyldithiocarbamate de sodium (NaCBM), ou vice-versa, 0.5-1.0 mg de NaCBM dans 20 ml de solution aqueuse peuvent être titrés hétérométriquement avec le nitrate de mercure(II).

Dans les deux cas, l'erreur est presque nulle. $Hg(CBM)_2$ insoluble est obtenu dans les deux cas.

ZUSAMMENFASSUNG

0.3—1.2 mg Quecksilber (= $Hg(NO_3)_2$ in 20 ml wässriger Lösung kann man heterometrisch mit Natriumdiäthyldithiocarbamat (NaCBM) titrieren. Umgekehrt kann man 0.5-1.0 mg NaCBM in 20 ml wässriger Lösung mit $Hg(NO_3)_2$ titrieren. In beiden Fällen ist der Fehler meistens gleich null und das unlösliche $Hg(CBM)_2$ wird erhalten.

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DETERMINATION OF TRACE QUANTITIES OF BORON WITH TWO NEW COLORIMETRIC REAGENTS

by

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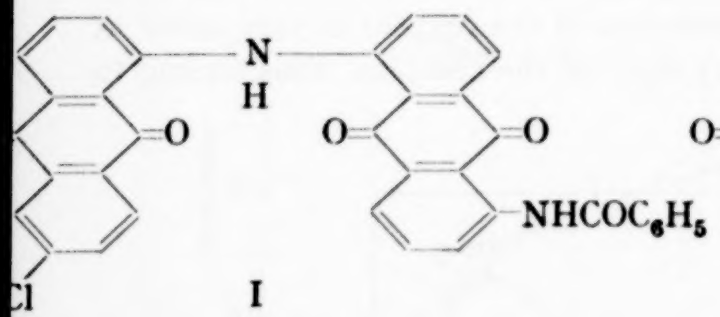
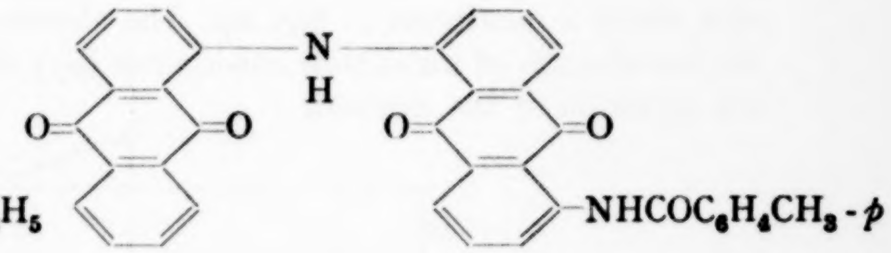
INTRODUCTION

Two new colorimetric methods for the determination of minute quantities of boron have been developed. The methods are based upon the formation of stable boron complexes of 5-benzamido-6′-chloro-1,1′-bis (anthraquinonyl)amine (Compound I) and 5-*p*-toluidino-1,1′-bis(anthraquinonyl)amine(Compound II), respectively, in concentrated (96%) sulfuric acid solution.



I



II

A procedure for rapidly decomposing the sample and subsequently separating the boron, as trimethyl borate, was also developed.

The results of this study show that the new methods are useful for the colorimetric determination of boron and that they have high sensitivities (Method I, 1 part of boron in 300 million parts of solutions; Method II, 1 part of boron in 200 million parts of solution), absorbance measurements being made in 1 cm cells at 635 mμ and 720 mμ, respectively.

Apparatus

All measurements were made with a Beckman spectrophotometer, Model DU, using matched 1-cm Corex cells.

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The distillation apparatus (Fig. 6) was constructed with Corning brand alkali Resistant Glass No. 7280. This brand of glassware was used because of its low boron content (maximum B_2O_3, 0.2%). "Blanks" indicated that there is no boron contamination from this type of glassware.

Pipets and volumetric flasks were of Kimble Brand glass.

A 250-watt G.E. Infrared Heat Lamp was employed for all evaporations.

Reagents

Compound I is a dark red solid and forms a greenish-yellow solution that turns to a deep red when heated at 130° C in 96% sulfuric acid. A $5 \cdot 10^{-3} M$ solution was prepared by dissolving 0.2910 g of reagent in 100 ml of 96% sulfuric acid. Solutions of lower concentrations were prepared by proper dilution with 96% sulfuric acid.

Compound II is also a dark red solid and forms a straw-colored solution that changes to a deep red when heated at 130° C in 96% sulfuric acid. A $1 \cdot 10^{-3} M$ solution was prepared by dissolving 0.0534 g of reagent in 100 ml of 96% sulfuric acid. Compounds I and II may be obtained from the LaMotte Chemical Products Co., Towson, Baltimore, Md. (U.S.A.).

A standard boron solution, containing 1.00 mg of boron per ml, was prepared by dissolving 0.5736 g of reagent grade *ortho* boric acid in 96% sulfuric acid to a volume of 100 ml. Boron solutions of lower concentrations were prepared by proper dilution with 96% sulfuric acid.

Stock solutions of the diverse ions were made with reagent grade compounds dissolved in 96% sulfuric acid. Each contained 1 mg of the desired ion per ml, except solutions of Fe^{+3}, Co^{+2}, Cu^{+2}, Mn^{+2}, Mg^{+2} and Cr^{+3} ions. Saturated solutions of the latter were used.

EXPERIMENTAL

Method I

Fig. 1 shows the absorbance curves of Compound I and of its colored boron complex. All measurements were made against 96% sulfuric acid as a blank. The complex shows a maximum at 635 mμ. The absorbance of the reagent is very small at the wavelength of maximum absorbance (635 mμ) of the complex, thus adding to the precision of the method.

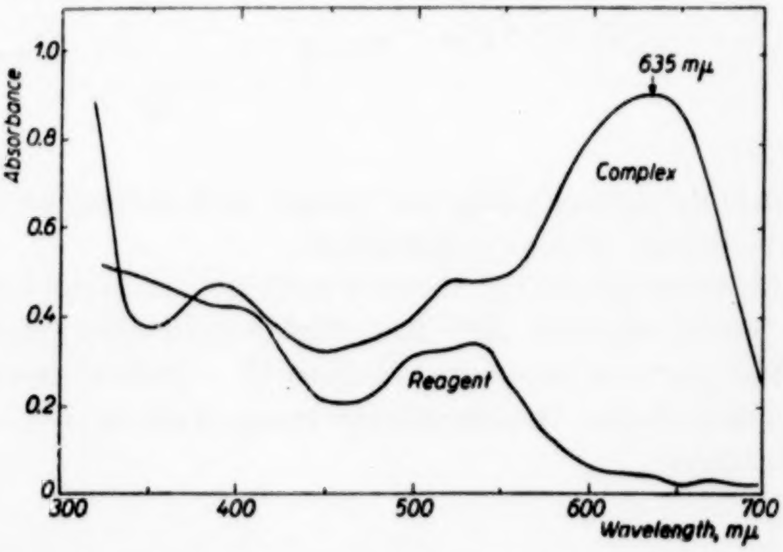


Fig. 1. Absorbance curves of Compound I and of its colored boron complex.

In order to evaluate the use of the boron complex maximum in the determination of small amounts of boron a study of the important properties of the absorption band was made.

Effect of sulfuric acid concentration. The colored complex shows considerable decrease in absorbance as the sulfuric acid concentration is decreased. The effect of sulfuric acid concentration was determined by measuring the absorbances of solutions containing 3.0 μg of boron, 1.0 ml of reagent, heating for 1 ½ hours at 130° C in an oven, and diluting to 10 ml volume with varying percentages of sulfuric acid. For precise results the acid content must be at least 96% by weight.

Rate of reaction and stability of complex. Because it is necessary to heat for several hours in order to develop full color intensity, the rate study was made at three temperatures: 100°, 130°, and 150° C. The study at 100° C showed a slow rate of formation for the boron complex. At 150° C a sharp increase in absorbance is obtained after a half hour, but with prolonged heating the absorbance decreases. At 130° C a sharp increase in absorbance is noted up to 1 ½ hours, after which no appreciable increase occurs. Upon standing for 59 days, the complex showed only a 3.4% increase in absorbance, a color stability quite adequate for analytical application.

The boron complex in solution. Three methods were employed to establish the empirical formula of the boron complex in solution. These were the mole ratio method of YOE AND JONES[1], the method of continuous variations introduced by JOB[2] and modified by VOSBURGH AND COOPER[3], and the slope ratio method recently proposed by HARVEY AND MANNING[4,5].

In applying the mole ratio method to the boron complex, solutions were prepared so that the reagent concentration was maintained constant at $2 \cdot 10^{-4} M$ and the ratio of moles of boron to moles of reagent varied from 0.5 to 4.0. A sulfuric acid blank was used in all measurements. The results in Fig. 2 indicate a one to one ratio.

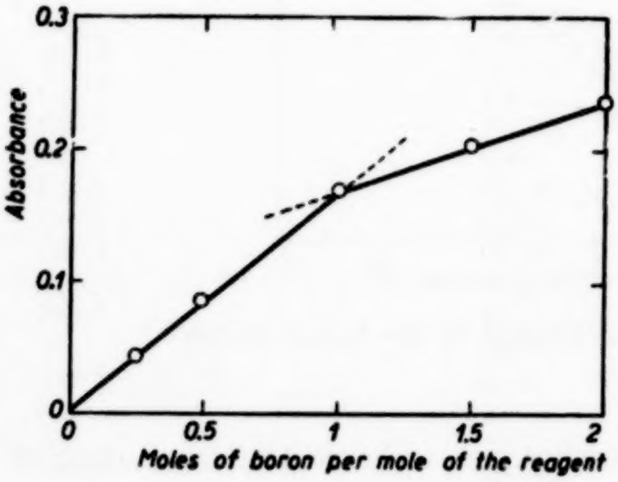


Fig. 2. Mole ratio method applied to the boron complex.

For the method of continuous variations, solutions were prepared containing x ml of a $1 \cdot 10^{-4} M$ reagent solution and $(5-x)$ ml of a $1 \cdot 10^{-4} M$ boron solution. The absorbances of these solutions *versus* a sulfuric acid blank were then measured at 635 mμ. The results are shown in Fig. 3. A maximum occurs at $x = 2.45$, so that $n = 1.04$, again indicating a reagent-to-boron ratio of 1:1.

In applying the slope ratio method, a series of solutions was prepared containing 20 γ of boron per 10 ml (an excess) and varying the concentration of the reagent. The absorbances were measured against a sulfuric acid blank. A second series was prepared $5 \cdot 10^{-4} M$ with respect to the reagent (an excess) and varying the amount of boron. The absorbances of this series were measured against a reagent blank. The results are shown in Fig. 4. From Fig. 4 $\text{slope}_1 = 1.620$ (boron in excess) and slope_2

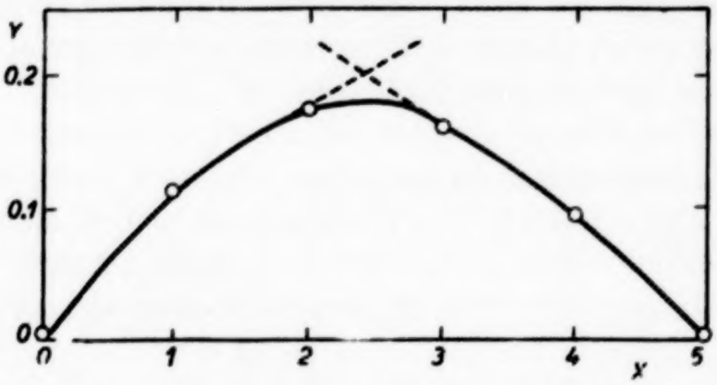


Fig. 3. Continuous variations method applied to the boron complex.

$= 1.680$ (reagent in excess). Hence the reagent-to-boron ratio is 1.03, a ratio in good agreement with the other two methods.

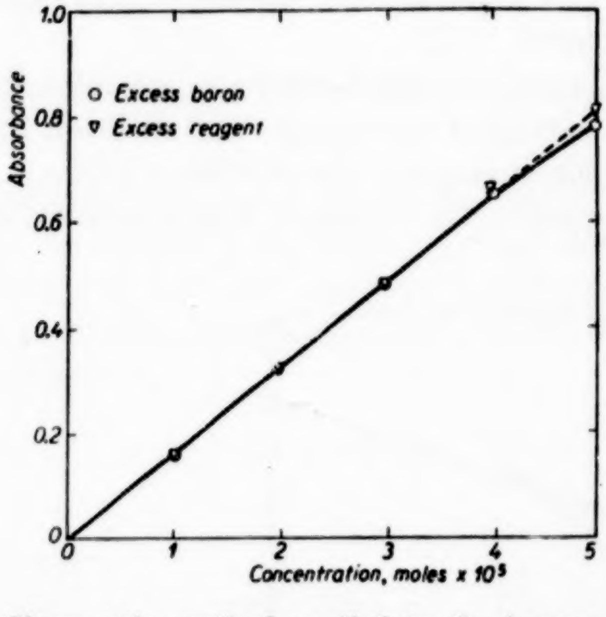
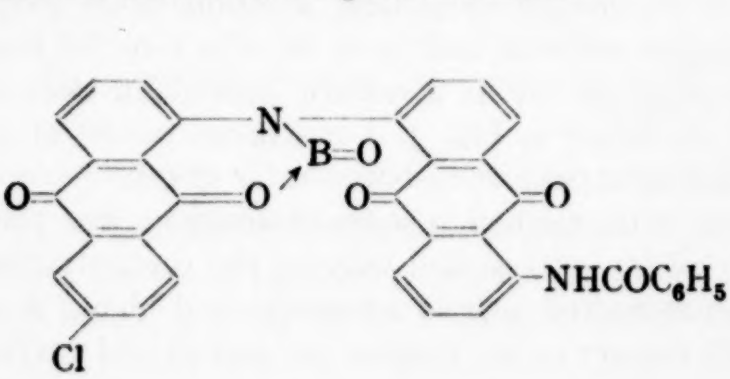


Fig. 4. Slope ratio method applied to the boron complex.

The results obtained by the three techniques indicate that one atom of boron reacts with one molecule of the reagent to form the complex. The following formula therefore is proposed for the boron complex *in solution.*



Beer's law and sensitivity. The boron complex obeys Beer's law over the concentration range of 1 to 5 γ of boron per 10 ml of solution, with a practical range of 1.2 to 4.2 γ, where the absorbances occur between 0.2 to 0.7 unit.

Using Sandell's[6] expression for the sensitivity of a colorimetric reaction and the absorbance of 0.05 p.p.m. of boron (0.097), the sensitivity is found to be 0.0005 γ per square centimeter. However, the practical sensitivity, determined by measuring the absorbance of decreasing amounts of boron, was found to be 0.003 γ per square centimeter, *i.e.*, 1 part of boron in 300 million parts of solution when absorbance measurement is made in a 1-cm cell.

Effect of diverse ions. To determine the interferences by diverse ions, individual solutions were prepared containing 0.3 p.p.m. of boron, the reagent, and 500 p.p.m. of each ion to be tested. An increase or decrease of 0.010 in absorbance (1.8%) was chosen arbitrarily to represent an interference. If interference was noted, then more tests were made using lower concentrations of the diverse ion, until a change of less than $\pm$ 0.010 absorbance unit was obtained.

This study shows that boron, especially when present in trace amounts, must be separated from many of the common metal ions, as well as oxidizing anions, before it can be determined accurately by this method. Table I lists the tolerances of the diverse ions investigated and the compounds employed in their preparation.

TABLE I

TOLERANCE TO DIVERSE IONS

Ion	*Added as*	*Limiting concentration p.p.m.*
Al^{+3}	Al_2O_3	500
AsO_4^{-3}	Na_3AsO_4	500
Ba^{+2}	$BaCl_2$	500
Ca^{+2}	$CaCl_2$	500
ClO_4^-	$KClO_4$	0
Cl^-	KCl	500
Cr^{+3}	$Cr_2(SO_4)_3$	0
Co^{+2}	$CoCl_2$	500
Cu^{+2}	$CuSO_4$	500
$C_2O_4^{-2}$	$Na_2C_2O_4$	<10
Fe^{+3}	$Fe_2(SO_4)_3$	0
F^-	CaF_2	0
Ge^{+4}	GeO_2	<3
IO_4^-	KIO_4	0
K^+	KCl	500
Mn^{+2}	$MnSO_4$	500
Na^+	$NaCl$	500
Ni^{+2}	$NiSO_4$	0
NO_3^-	KNO_3	0
NO_2^-	$NaNO_2$	0
PO_4^{-3}	$Ca_3(PO_4)_2$	0
$Sb_2O_7^{-4}$	$K_2H_2Sb_2O_7$	500
Sr^{+2}	$SrCO_3$	500
Zn^{+2}	$ZnCl_2$	500

Method II

Fig. 5 shows the absorbance curves of Compound II and of the boron complex of compound II. All measurements were made against 96% sulfuric acid as a blank.

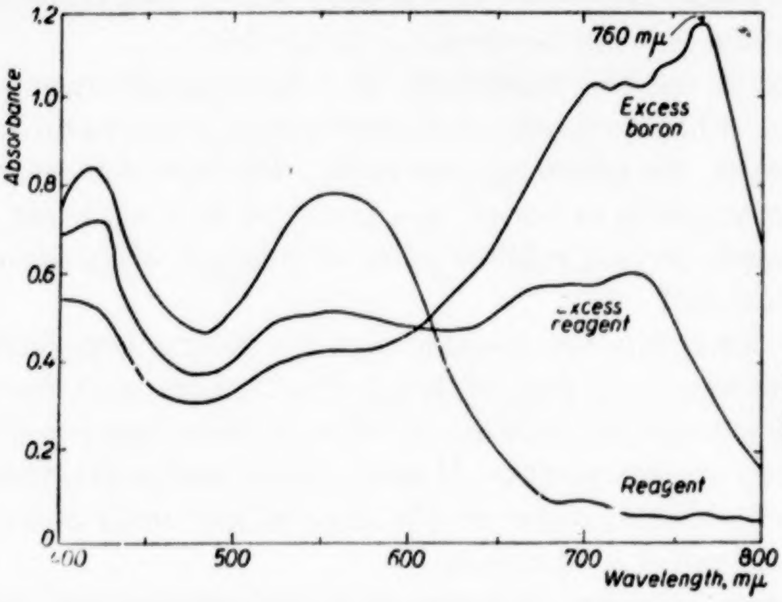


Fig. 5. Absorbance curves of Compound II and of its colored boron complex.

The colored complex has a maximum at 720 mμ when excess reagent is present and one at 760 mμ when excess boron is present. This shift in the maximum, when one or the other substance is varied in excess, is attributed to the formation of more than one complex.

In order to evaluate the use of the boron complex maximum (at 720 mμ) as a means of determining small amounts of boron, a study was made of some of its important properties.

Effect of sulfuric acid concentration. The effect of the sulfuric acid concentration was determined by measuring the absorbances of solutions containing 4.0 γ of boron, 1.0 ml of reagent, heating for three hours at 130° C in an oven, and diluting to 10 ml volume with varying percentages of sulfuric acid. The results of this study proved to be the same as those for Compound I, *i.e.*, the sulfuric acid strength must be at least 96%.

Rate of reaction and stability of complex. The study on the rate of the reaction was carried out in the same manner as for Compound I. Results showed that the solutions must be heated for three hours at 130° C. Upon standing for 17 days, the complex showed only a 3.3% increase in absorbance, a color stability quite adequate for analytical use.

The boron complex in solution. The three methods mentioned above[1-5] were used in an attempt to establish the empirical formula of the complex *in solution.* All results were unsatisfactory. They indicate, however, that more than one complex exists and hence the two maxima obtained in Fig. 5.

Beer's law and sensitivity. The boron complex obeys Beer's law over the concentration range of 1 to 4 γ of boron per 10 ml of solution, with a practical range of 0.95 to 3.8 γ, where the absorbances occur between 0.2 to 0.7 unit.

Using SANDELL's[6] expression for the sensitivity of a colorimetric reaction and the absorbance of 0.05 p.p.m. of boron (0.105), the sensitivity is found to be 0.0004 γ per square centimeter. However, the practical sensitivity, determined by measuring the absorbance of decreasing amounts of boron, was found to be 0.005 γ per square centimeter, *i.e.*, 1 part of boron in 200 million parts of solution when absorbance measurement is made in a 1-cm cell.

Effect of diverse ions. This study was carried out in the same manner as described above for Compound I. Tolerances to diverse ions were the same as those shown in Table I.

SEPARATION OF BORON

GOOCH[7] found that alkali and alkaline-earth borates, on being distilled with absolute (acetone-free) methyl alcohol, give up their boron in the form of methyl borate, a liquid which boils at 65° C. If the methyl borate is brought into contact with a weighed amount of base in the presence of water, it is completely hydrolyzed. If, however, a small excess of base is not present, the ester will be converted to the unstable sodium metaborate[8] instead of the stable sodium borate and boron will be lost when the distillate is evaporated.

The fact that comparatively small amounts of boric acid can be volatilized quantitatively from a methanol solution is probably due to the formation of complex compounds with the solvent molecules, the complexes being as volatile as the solvent itself. There is little question of forming an ester with HO-radicals and boric acid. This reaction involves the liberation of one molecule of water and the formation of a complex, the processes being very rapid and having properties of ester formation.

Esters of boric acid differ from most esters because they combine with one mole of an alcohol to give a monobasic acid[9]. This occurs because the boron atom lacks a pair of electrons. Thus, it can form a complex with a molecule of the alcohol by taking an unshared pair of electrons from the oxygen atom into its valence shell. This electron pair is held so strongly that the proton can be readily removed.

Standard leaf sample. In order to determine the conditions for the decomposition of the sample and the subsequent separation of the boron, it was necessary to have a large supply of a green leafy substance the boron content of which was accurately known. This was accomplished by procuring a large amount of spinach (2.72 kilograms), which is as representative of a boron-containing substance as any other green leafy vegetable. This spinach was dried under heat lamps until the moisture was removed. The crisp, dried leaves were crushed and ground in a large porcelain mortar with pestle. The crushed leaves were then mixed, so as to yield a homogeneous mixture, and stored in a large desiccator over P_2O_5. The boron content was then accurately

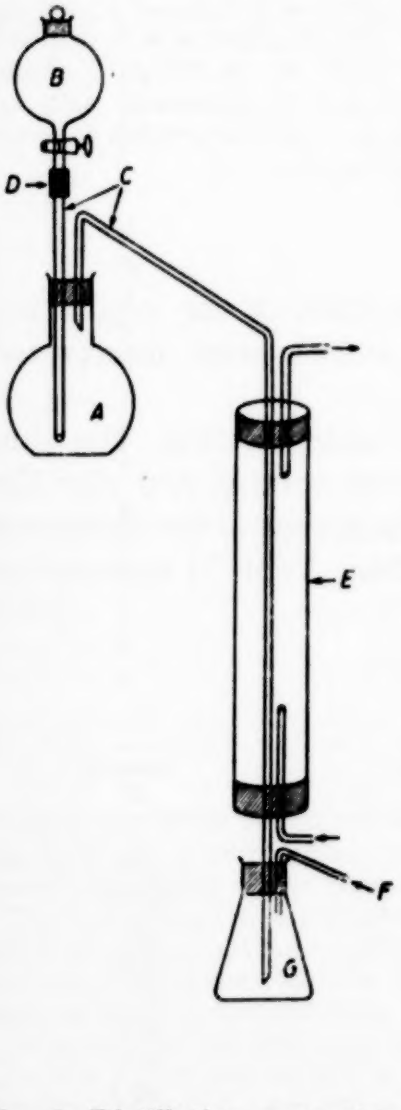


Fig. 6. Distillation apparatus.
A 200 ml boron free flask
B dropping funnel
C 8 mm boron free glass tubing
D polyethylene seal
E condenser (borosilicate glass)
F capillary tube exit
G 250 ml boron free flask

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determined. For this the titration of boric acid, in the presence of mannitol, was chosen. The ashing technique used was that prescribed by the A.O.A.C.[10]. The titrations were carried out with a Fisher Titrimeter equipped with a calomel-glass electrode system. The details of the titrations accord with those of HILLEBRAND AND LUNDELL[8].

The sodium hydroxide solution used in the determination of the boron content of the standard leaf sample was standardized against samples of pure orthoboric acid.

Five samples of the dried spinach were titrated and gave values of 77.0, 74. 0, 73.4, 71.1 and 70.0 p.p.m. of boron, respectively; an average value of 73.1 p.p.m.

PROCEDURE

Approximately 0.1 g samples are used for each analysis, depending on the boron content. The procedure is as follows: into a distilling flask (Fig. 6), the following substances are added — leaf sample, 1 g of calcium hydroxide, and 2 ml of 96% sulfuric acid. The flask is then connected to the distillation system. The receiving flask, containing 1 ml of 0.01 *N* sodium hydroxide and 25 ml of distilled water, is then connected to the system. Two milliliters of 30% hydrogen peroxide are cautiously added to the distilling flask through the dropping funnel. When all organic matter has been destroyed, a paraffin bath is placed in contact with the flask. Then 100 ml of absolute methanol is added. The temperature of the bath is slowly raised to approximately 90° C, giving a slow but steady volatilization of the ester and excess methanol. The distillation is continued until no more liquid comes over. Remove the receiving flask, add 5 ml of *N* NH_4OH, shake well and evaporate the solution to dryness on a hot-plate (set on low temperature) with an infrared lamp suspended about 4 inches above the mouth of the flask. Cool the residue to room temperature, add the reagent solution, mix and measure the absorbance.

STANDARD DEVIATION

In order to determine the precision and standard deviation of the separation of boron by the new technique, a set of experimental values were interpreted statistically.

The results of twelve distillations were used for the interpretation. The sum of the squares of the 12 results, in per cent recovery, was totaled and also the square of the sum of the 12 results divided by *n*. The square root of the difference of these results divided by *n*-1 gives the standard deviation. Table II summarizes the data.

TABLE II

STANDARD DEVIATION DATA

Distillation No.	*Boron present* µg	*Boron found* µg	*Recovery* %
1	5.80	5.78	99.6
2	5.20	5.20	100.0
3	4.90	4.86	99.2
4	4.75	4.65	97.9
5	4.50	4.40	97.8
6	5.09	5.00	98.2
7	5.46	5.40	98.9
8	5.66	5.63	99.5
9	6.37	6.34	99.5
10	5.46	5.42	99.3
11	5.36	5.30	98.9
12	5.15	5.05	98.1
		Av.	98.9

Standard deviation: 0.58%

APPLICATION OF PROCEDURE

Table III summarizes the results of five referee samples; four fruit tree leaves and one sample of alfalfa. The samples were obtained from the School of Agriculture, Michigan State College, East Lansing, Michigan. Our laboratory is one of about twenty cooperating in this referee program. These laboratories are located throughout the U.S.A.

TABLE III

RESULT OF ANALYSES OF STANDARD REFEREE SAMPLES

Sample type	*Referee values*	*Boron found*	*Average*
	p.p.m.	p.p.m.	p.p.m.
Apple —1	20.0—34.5	26.0	
—2		28.8	
—3		25.8	
—4		26.7	
—5	av. 27.0	29.8	27.4
Cherry—1	29.5—45.8	35.2	
—2		38.0	
—3		36.4	
—4		39.0	
—5	av. 37.0	38.6	37.4
Citrus —1	28.0—85.0	60.0	
—2		54.2	
—3		69.3	
—4		62.0	
—5		59.5	
—6	av. 64.0	67.3	62.0
Peach —1	17.0—50.0	42.0	
—2		36.0	
—3		40.0	
—4		33.4	
—5		35.0	
—6	av. 36.0	44.0	38.4
Alfalfa—1	26.8—35.0	32.0	
—2		31.6	
—3	av. 32.0	32.8	32.1

SUMMARY

Two new color reactions with boron are reported. Sensitive methods have been developed for their use. A new method for the decomposition of fruit tree leaves and alfalfa, and the subsequent separation of the boron is described.

The reagents are 5-benzamido-6′-chloro-1,1′-bis (anthraquinonyl) amine(I) and 5-*p*-toluidino-1,1′-bis (anthraquinonyl) amine(II). Concentrated (96%) sulfuric acid is used as the solvent. The formation of the boron complex of the reagents was found to be dependent on the following variables: time of heating, temperature, sulfuric acid content and the presence of diverse ions.

Solutions of the two complexes follow Beer's law over the boron range indicated: Compound I, 0 to 0.5 γ at wavelength of 635 mμ and Compound II, 0 to 0.4 γ at wavelength 720 mμ. The sensitivities are 1 : 300,000,000 and 1 : 200,000,000, respectively. The standard deviation was calculated for the determination of boron with each compound. Results showed 0.002 absorbance unit, *i.e.*, 0.001 γ of boron for Compound I and 0.005 absorbance unit, *i.e.*, 0.002 γ of boron for Compound II.

The method of decomposing the leaves and alfalfa samples is based upon destroying all the organic matter with a mixture of 96% sulfuric acid and 30% hydrogen peroxide within the distilling flask. Boron is then distilled off as the volatile trimethyl ester. The standard deviation of the method is 0.58%.

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RÉSUMÉ

Deux nouvelles réactions colorées du bore sont décrites. Des méthodes sensibles ont été mises au point pour leur emploi. Une nouvelle méthode est donnée pour la minéralisation des feuilles d'arbres fruitiers et de luzerne et pour la séparation du bore.

Ces réactifs sont: la 5-benzamido-6-chloro-1,1'-bis (anthraquinone) amine (I) et la 5-*p*-toluidino-1,1'-bis (anthraquinone) amine (II). L'acide sulfurique concentré (96%) est utilisé comme solvant. La formation des complexes de ces réactifs avec le bore dépend des facteurs suivants: durée du chauffage, température, teneur en acide sulfurique et présence de divers ions.

Les solutions de ces deux complexes suivent la loi de Beer pour les quantités de bore suivantes: composé I, 0 à 0.5 γ à la longueur d'onde de 635 mμ et composé II, 0 à 0.4 γ à 720 mμ. Les sensibilités sont respectivement: 1 : 300,000,000 et 1 : 200,000,000. L'erreur a été calculée pour le dosage du bore avec chacun de ces composés. Les résultats ont donné 0.002 unité d'absorption, c'est-à-dire 0.001 γ de bore pour le composé I et 0.005 unité d'absorption, c'est-à-dire 0.002 γ de bore pour le composé II.

La méthode de minéralisation des feuilles et de la luzerne est basée sur la destruction de la matière organique par un mélange d'acide sulfurique à 96% et de peroxyde d'hydrogène à 30% dans un ballon à distiller. Le bore est ensuite distillé sous forme de son triméthylester volatil. L'erreur est de 0.58%.

ZUSAMMENFASSUNG

Es werden zwei neue Farbreaktionen für Bor beschrieben. Es wurden empfindliche Methoden für ihre Anwendung ausgearbeitet. Eine neue Methode für die Mineralisation von Obstbaumblättern und von Luzernen und für die Abtrennung von Bor wird gegeben.

Diese Reagenzien sind: das 5-Benzamido-1,1'-bis(anthrachinon) amine (I) und das 5-*p*-Toluidino-1,1'-bis (anthrachinon) amin (II). Konzentrierte Schwefelsäure (96%) wird als Lösungsmittel verwendet. Die Bildung der Komplexe dieser Reagenzien mit dem Bor, hängt von folgenden Faktoren ab: Dauer des Heizens, Temperatur, Gehalt an Schwefelsäure und Gegenwart von verschiedenen Ionen.

Die Lösungen dieser beiden Komplexe folgen dem Beerschen Gesetz für folgende Bormengen: Verbindung I, 0 bis 0.5 γ bei der Wellenlänge 635 mμ und Verbindung II, 0 bis 0.4 γ bei 720 mμ. Die Empfindlichkeiten sind respektive: 1 : 300,000,000 und 1 : 200,000,000. Der Fehler wurde für die Bestimmung von Bor mit beiden Verbindungen berechnet. Die Resultate ergaben 0.002 Absorptionseinheit, d.h. 0.001 γ Bor für die Verbindung I und 0.005 Absorptionseinheit, d.h. 0.002 γ Bor für Verbindung II.

Die Methode der Mineralisation der Blätter und der Luzernen basiert auf der Zerstörung der organischen Substanzen mittels einer Mischung von Schwefelsäure zu 96% und Wasserstoffperoxyd zu 30% in einem Destillationskolben. Das Bor wird darauf in Form seines flüchtigen Trimethylesters destilliert. Der Fehler ist 0.58%.

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UNE MÉTHODE DE DOSAGE COLORIMÉTRIQUE DU PHOSPHORE DANS LES MATIÈRES ORGANIQUES

par

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INTRODUCTION

Pour doser une très petite quantité de phosphore, soit dans les matières organiques, soit dans les eaux naturelles, il faut d'abord minéraliser les échantillons et ensuite contrôler l'acidité et la concentration des sels de la solution à analyser. Cet exposé a pour but 1° de présenter un nouveau flacon de destruction des matières organiques permettant de minéraliser les échantillons sans aucun soubresaut; 2° de proposer l'emploi de l'oxyde hydraté de fer(III) pour la séparation du phosphate des autres sels présents. LEVINE *et al.*[1] indiquent l'utilisation possible de l'oxyde hydraté d'aluminium pour le dosage colorimétrique des phosphates dans l'eau.

PARTIE EXPÉRIMENTALE

Flacon de destruction des matières organiques

Pour éviter des pertes dues aux soubresauts lors de la minéralisation des matières organiques au moyen du flacon de Kjeldahl, K. IWASAKI[2] proposa un nouveau récipient.

Nous proposons ici l'utilisation d'un flacon (Fig. 1) où A est un tube en verre, B le flacon et C le réfrigérant présenté par SCHIRM[3]. A l'extrémité inférieure de A est fixé un tube ouvert, qui agit comme de la pierre ponce.

Mode opératoire

On introduit l'échantillon dans le flacon, on ajoute successivement 2 ml d'acide sulfurique (densité: 1.84), 5 mg de fer(III) (solution de chlorure de fer(III)) et 0.2 ml d'acide perchlorique. On chauffe le flacon en prenant garde à ne pas volatiliser l'acide sulfurique; on utilise un réfrigérant de SCHIRM[3]. La minéralisation est complète après deux heures, la présence du sel de fer(III) favorise considérablement la destruction.

On verse la liqueur après minéralisation complète dans un bécher de 100 ml et on ajoute 70 ml d'eau environ. On chauffe la solution à 70-80° C et on la neutralise par l'ammoniaque $4N$, en employant le pourpre de bromocrésol comme indicateur. On agite. Après refroidissement, on

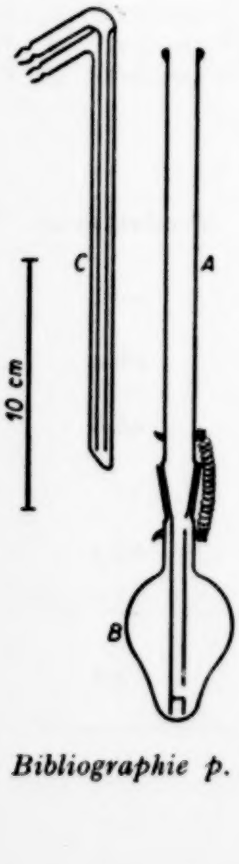

Fig. 1. Flacon à destruction des matières organiques.

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filtre le précipité à l'aide d'un filtre de verre. On dissout le précipité dans 15 ml d'acide sulfurique *N*. On ajoute 1 ml de solution de molybdate d'ammonium à 2% et 1 ml de sulfate d'hydrazine à 0.5%; on complète la solution à 25 ml avec de l'eau distillée. On chauffe au bain-marie pendant 30 minutes (formation de bleu de molybdène) et on refroidit. On mesure la densité optique à 840 mμ ou 700 mμ à l'aide d'un spectrophotomètre.

Courbe d'étalonnage

Nous donnons la courbe d'étalonnage obtenue (Fig. 2).

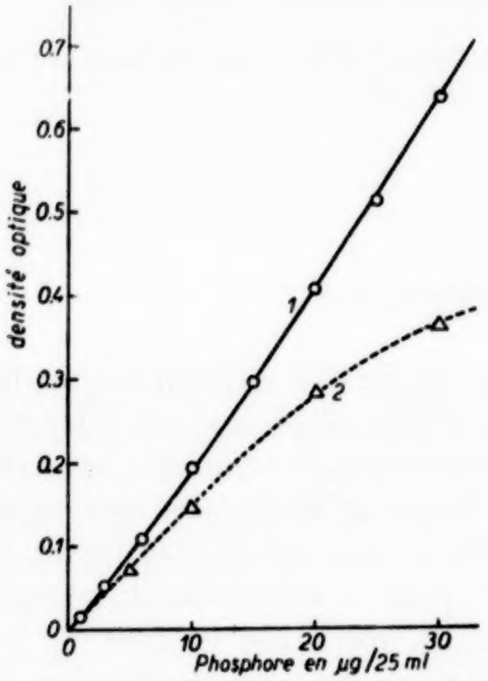

Fig. 2. Courbe d'étalonnage. Cuvette: 16 mm; longueur d'onde: 700 mμ. Courbe 1: cette méthode. Courbe 2: sans emploi de la précipitation de $Fe(OH)_3$.

On donne également la courbe obtenue sans utiliser d'oxyde hydraté, comme collecteur de phosphate (on neutralise la solution minéralisée et on opère comme précédemment).

Exemples d'analyse

Comme on le voit dans le Tableau I, la méthode est quantitative.

TABLEAU I

EXEMPLES D'ANALYSE

Échantillon	*Quantité prise*	*P ajouté en µg*	*P retrouvé en µg*	*P calculé en µg*
Aiguille du pin (matière séchée)	10 mg	—	8.4	—
id.	10 mg	10	18.1	18.4
Oeuf de *Rana japonica*	1	—	18.8	—
id.	1	10	28.5	28.8
Eau d'un puits dans la Falculté des Sciences de Nagoya	125 ml	—	23.0	—
id.	125 ml	2.5	25.7	25.5
Eau du Courant Noir (Superficie) (34°51'N, 139°59'E)	200 ml	—	2.2	—
id.	200 ml	5	7.3	7.2

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On peut l'appliquer aux échantillons d'eaux naturelles, dont quelques exemples sont donnés dans le même tableau.

Nous tenons à mentionner le nom du Professeur K. SUGAWARA, à qui va notre profonde gratitude pour son intérêt particulier et son encouragement incessant au cours de ces recherches.

RÉSUMÉ

1° On propose l'emploi de l'oxyde hydraté de fer(III) pour la séparation du phosphate dans une solution contenant d'autres sels.

2° On présente un nouveau flacon de destruction des matières organiques permettant de minéraliser les échantillons sans aucun soubresaut.

3° En employant l'oxyde hydraté de fer(III) et le nouveau flacon, on peut effectuer avec succès le dosage du phosphore, soit dans les matières organiques, soit dans les eaux naturelles.

SUMMARY

1° The use of hydrated ferric oxide is suggested for separating phosphate from a solution containing other salts.

2° A new flask is proposed, which can be used in the decomposition of organic matters. By means of this flask, we can carry out the mineralization without any bumping.

3° By using hydrated ferric oxide and the new flask, we can successfully carry out the determination of phosphorus in natural waters as well as in organic matter.

ZUSAMMENFASSUNG

1° Die Verwendung des Ferrihydroxyds für die Abtrennung des Phosphates aus einer, auch andere Salze enthaltenden Lösung wurde vorgeschlagen.

2° Eine neue Flasche wurde beschrieben, die für die Zersetzung der organischen Substanzen gebraucht wird. Mittels dieser Flasche kann die Mineralisierung ohne Stossen ausgeführt werden.

3° Durch Anwendung des Ferrihydroxyds und der neuen Flasche, kann der Phosphor in organischen Substanzen und in natürlichem Wasser erfolgreich bestimmt werden.

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COLORIMETRIC DETERMINATION OF GLUTAMIC ACID IN PROTEIN HYDROLYSATES

by

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A colorimetric method for the determination of glutamic acid in protein hydrolysates was described in a previous communication[1]. The method was based on a colour reaction given by pyrrolidonecarboxylic acid on heating with hydroxylamine and subsequent treatment with ferric chloride. Since glutamic acid is almost completely converted into pyrrolidonecarboxylic acid at 125° and pH 3-4, this colour reaction can be used for the quantitative determination of glutamic acid in protein hydrolysates.

The method presented here is based on the findings of SACHS AND BRAND[2] that the lactone formed on treating glutamic acid with nitrous acid can be estimated colorimetrically by the procedure described by HESTRIN[3]. We found that as little as 2/3 of a micromole of glutamic acid could be determined accurately by this method using a Klett-Summerson photoelectric colorimeter.

Glutamic acid contained in protein hydrolysates was adsorbed (together with aspartic acid) on Amberlite IR-4B columns at pH 3-4 and subsequently eluted with N hydrochloric acid as described by MORRIES AND STUCKEY[4]. The eluates were treated with nitrite and the lactone formed from glumatic acid estimated colorimetrically by HESTRIN's procedure. The values obtained with various proteins were in good agreement with those obtained by the colorimetric method previously described[1].

EXPERIMENTAL

2 g of protein were hydrolysed by refluxing with 20 ml of hydrochloric acid (1:1) in a stirred oil bath at 120-125° for 35 hours. 1 g of purified charcoal was added and heating continued for 1 hour. After cooling, water was added, the hydrolysate filtered and the residue washed with water. The filtrate was concentrated *in vacuo*, some water added and the solution was again evaporated *in vacuo*, this procedure being repeated 1 or 2 times. The dry residue was dissolved in water to a volume of 50 ml. 5 ml aliquots were adjusted to pH 3.5-4 by addition of 3.5N NaOH and water was added to a volume of 15 ml. 5 ml of this solution was transferred to the top of an Amberlite IR-4B column, prepared in the manner described by MORRIS AND STUCKEY[4]. The resin (mesh size 40-60) was treated with dilute hydrochloric acid and washed with water by decantation until the pH of the washing was 3-4. The resin was then transferred to a glass tube of about 1 cm internal diameter to a height of 15 cm and again washed with water until the pH of the effluent was between 3 and 4. The hydrolysate sample was allowed to run through the column at a rate of 1-2 ml per minute. The effluent was again passed through the column, which was then washed

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with water (about 40 ml) until a portion of the washings no longer gave a colour reaction with ninhydrin. The adsorbed aminodicarboxylic acids were eluted with 100 ml of N HCl. The eluate was concentrated to dryness *in vacuo* and the residue dissolved in water (total volume 25 ml). In accordance with the procedure employed by SACHS AND BRAND[2], a 5 ml portion of this solution was transferred to a 25 ml volumetric flask, 1 ml of glacial acetic acid and 2 ml of sodium nitrite solution (800 g sodium nitrite per liter of water) were added and the mixture maintained at 25° for 10 minutes. 10 ml of $2M$ hydroxylamine hydrochloride was added dropwise whilst cooling the flask with ice water. The flask was filled up to the mark with water. 3 ml aliquots of this solution were added to a solution containing 1 ml of $2M$ hydroxylamine hydrochloride and 2 ml of $3.5N$ NaOH. After 4 minutes, 1.65 ml HCl (1:2) was added (the pH being now 1-1.2) and the mixture brought to a final volume of 10 ml by addition of a $0.37M$ solution of ferric chloride in $0.1N$ HCl. The colour produced was immediately measured in a Klett-Summerson photoelectric colorimeter with filter No. 54. For comparison, standard glutamic acid (or glutamic acid hydrochloride) solutions were treated in the same manner as the solutions of the concentrated eluates. The results obtained with various amounts of glutamic acid are given in Fig. 1. A complete recovery of glutamic acid was obtained when its standard solutions were passed through Amberlite IR-4B columns subsequently eluted with N HCl.

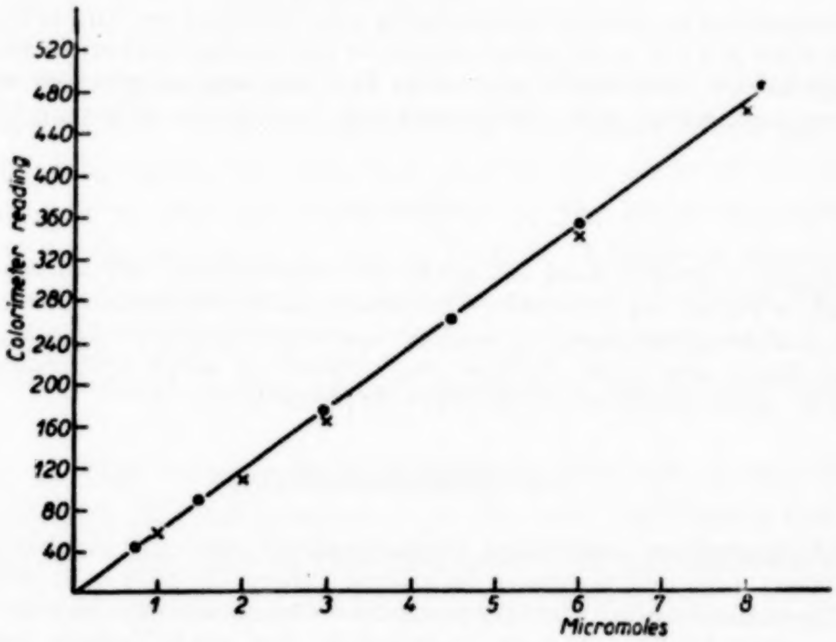

Fig. 1. Optical density (Klett-Summerson colorimeter reading) of hydroxamic acid-iron complex obtained from a) glutamic acid treated with nitrous acid (•); b) succinic anhydride (x).

The figures given in TABLE I are average values obtained from 3 separate hydrolysates of each protein. The results were calculated for the dry protein. Moisture was estimated by drying the proteins *in vacuo* over phosphorus pentoxide at 100°.

TABLE I

GLUTAMIC ACID CONTENT OF PROTEINS (PER CENT)

Protein	*Found*	*Previous findings*[1]
Casein*	22.1	23.1
Edestin**	20.5	20.0
Zein**	26.3	25.3
Fibrin**	15.7	16.5

* Fat free, The British Drug Houses Ltd., London.
** Nutritional Biochemicals Corporation, Cleveland, Ohio.

It may be of interest to note that the values obtained for glutamic acid by the colorimetric method correspond closely to those given by succinohydroxamic acid as indicated in Fig. 1. The values for succinohydroxamic acid were obtained as follows. A stock solution of succinohydroxamic acid was prepared by the procedure of LIPMANN AND TUTTLE[5]. Hydrochloric acid and water were added to aliquots containing various amounts of succinohydroxamic acid to produce a pH of 1-1.2 and a final volume of 7.65 ml. Ferric chloride was added to a final volume of 10 ml and the colour produced measured as in the glutamic acid determination. It may be recalled that glutamohydroxamic acid was found to give colorimetric values with ferric chloride which were quite close to those obtained with succinohydroxamic acid[6].

SUMMARY

Glutamic acid contained in protein hydrolysates was adsorbed on Amberlite IR-4B columns at pH 3-4 and eluted with *N* HCl. Addition of nitrite to the eluates converted glutamic acid into the corresponding lactone of hydroxyglutaric acid. Hydroxylamine reacted with this lactone to give a hydroxamic acid, which was determined colorimetrically following the addition of ferric chloride.

RÉSUMÉ

L'acide glutamique, contenu dans les protéines hydrolysées, est adsorbé sur des colonnes d'Amberlite IR-4B à un pH 3-4 et ensuite élué avec l'acide chlorhydrique normal. L'addition de nitrite convertit l'acide glutamique en lactone correspondante de l'acide hydroxyglutarique. L'hydroxylamine réagit avec cette lactone en donnant un acide hydroxamique que l'on dose colorimétriquement après addition de chlorure de fer(III).

ZUSAMMENFASSUNG

Die in Proteinhydrolysaten enthaltene Glutaminsäure wird auf Amberlite-IR-4B-Kolonnen bei pH 3-4 adsorbiert und mit normaler Salzsäure eluiert. Zugabe von Nitrit zu den Eluaten verwandelt die Glutaminsäure in das entsprechende Oxyglutarsäurelakton. Letzeres wird durch Hydroxylamin in eine Hydroxamsäure verwandelt, die nach Zugabe von Eisen(III)-chlorid kolorimetrisch bestimmt wird.

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HIGH-FREQUENCY INSTRUMENTATION*

by

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INTRODUCTION

High-frequency titrations are carried out in a dielectric vessel having external metal electrodes connected to a high-frequency oscillator. The metal electrodes are separated from the solution in the titration cell by the walls of the titration vessel, usually glass. Changes in the conductivity or in the dielectric constant (specific inductive capacity) of the solution in the cell cause changes in the oscillator circuit which can be measured and plotted against the volume of titrant added. The principles of high-frequency titrimetry have recently been reviewed by a number of authors [1,2,6,8,9,11,12]. Several studies of high-frequency titration cell parameters have been made[3,8,9].

A disadvantage of high-frequency titrimeters is that the sensitivity to concentration changes depends on the geometry of the cell containing the sample being titrated, as well as the frequency of the instrument. In the present work the effect of cell geometry on the region of sensitivity was investigated.

Apparatus

The high-frequency instruments used were the commercially available Sargent Chemical Oscillometer Model V[11] and a laboratory-built apparatus based on a crystal oscillator circuit[4]. The Oscillometer responds primarily to changes in the effective capacitance in the titration cell circuit. The other titrimeter was designed to respond to either effective capacitance, or to effective conductance changes in the titration cell circuit. A change in electrolyte concentration causes a change in grid bias voltage which is measured with a voltmeter. A cell adapter consisting of variable capacitors and single-pole double-throw switches in a metal cabinet permitted various types of cells to be used with either instrument[5].

High-frequency conductivity cell

A high-frequency cell may be considered in terms of its equivalent electrical circuit, shown in Fig. 1, A. R_s and C_s represent the resistance and capacitance which would exist in the cell circuit if the metal electrodes were in contact with the solution. C_c is composed of two capacitors in series, each having one of the metal electrodes for one plate, the wall of the glass vessel for a dielectric and the surface of the solution in contact with the glass for another plate.

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* This paper was presented at the Instrumentation Symposium of the Electronics Division of the Electrochemical Society, Chicago, May, 1954.

R_s and C_s vary with the resistivity and dielectric constant, respectively, of the solution in the cell. C_c is constant for a given cell. For a titration cell with electrodes of the same size and shape, the value of C_c varies directly as the area of the metal electrodes and the dielectric constant of the material of which the container is constructed and inversely as the thickness of the wall of the container.

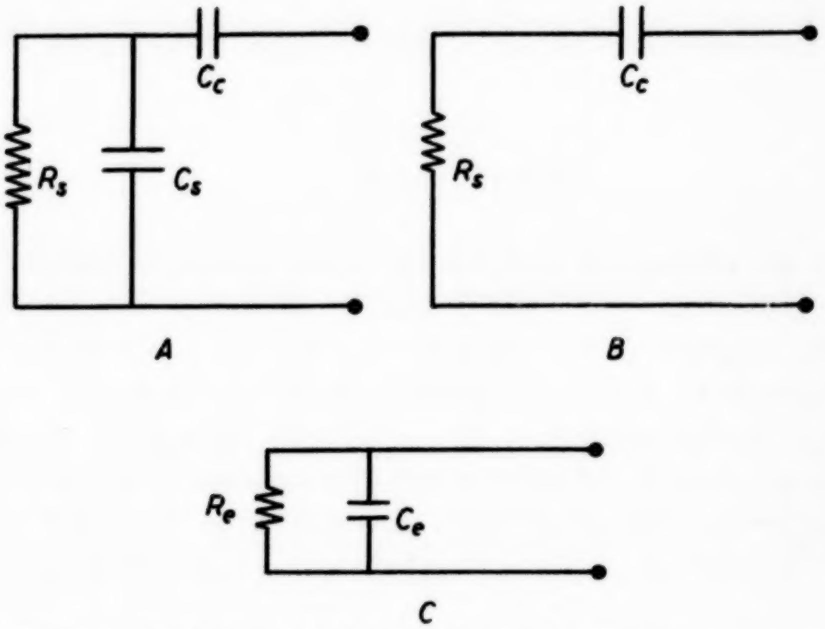

Fig. 1. Equivalent high-frequency cell circuits.
A. Equivalent electrical circuit of a high-frequency cell.
B. Simplified series equivalent circuit.
C. Simplified parallel equivalent circuit.

A cell was constructed having physical dimensions such that C_s was made insignificant. For this cell the simplified series equivalent circuit, Fig. 1, B, applies. This was accomplished by using a long, narrow glass tube as the solution container with two thin metal bands as outer electrodes. The capacitor C_s then consisted effectively of two thin discs separated by a dielectric. From the equation for parallel plate capacitors,

$$C_s = \frac{K_s A}{4 \pi d} \tag{1}$$

it is seen that, although the dielectric constant (K_s) of the interspace is that of the solution, the area (A) of the plates is quite small and the distance between the plates (d) is large, so that C_s is made to approach zero. This arrangement would have a relatively large edge effect but the fringing would have no influence on the value of C_s since this part of the field passes through air. The overall effect, therefore, is equivalent to three capacitances in parallel. Two of these represent capacitors having air and glass as dielectrics and are constant for a given cell. Only C_s changes with the dielectric constant of the solution, and the value of C_s is made to approach zero.

Since C_c is constant for a given titration cell and effectively the only variable in the simplified series equivalent circuit is R_s, this cell should respond almost wholly to changes in the conductivity of the solution. Changes in the dielectric constant of the sample solution should have no appreciable effect on the equivalent circuit. Such a cell was tested with benzene, 1,4-dioxane, chloroform, acetone, methyl alcohol, distilled water, $0.001 N$ and $0.1 N$ potassium chloride, saturated sodium chloride, concentrated hydrochloric acid and mercury. The value of C_s with water (25° C) as dielectric was about 1% of the value of C_c. Recently a similar conductivity cell has been used for the radio-frequency measurement of the salinity of ocean water[7].

Response curves

The response curve of a high-frequency titration apparatus is a plot of the property measured by the instrument *versus* the normality or electrolytic conductance of the solution contained in the titration cell. Response curves of instrument readings *versus* dielectric constant can be made. Instruments, like the Sargent Oscillometer, which measure changes in effective capacity in the titration cell circuit display an S-shaped response curve, whereas the instruments which measure conductance loss show a U-shaped curve.

The basis for these response curves can be seen by a consideration of the simplified series equivalent cell circuit shown in Fig. 1, B. In this circuit R_s is inversely proportional to the electrolytic conductance of the solution in the titration cell. C_c is constant for a given titration cell.

The impedance of the titration cell circuit may be measured at the terminals of the titration cell in terms of the parallel admittance components, conductance and capacitive susceptance. The equivalent circuit of Fig. 1, B is shown in Fig. 1, C in terms of the parallel admittance components. R_e and C_e are the effective parallel resistance and capacitance of the simplified series equivalent titration cell circuit.

Equations relating C_e and R_e to C_c and R_s in the simplified series equivalent circuit are given below[10].

$$C_e = \frac{1}{4\,\pi^2\,f^2\,C_c\left[R_s^2 + \dfrac{1}{4\,\pi^2\,f^2\,C_c^2}\right]} \tag{2}$$

$$R_e = \frac{R_s^2 + \dfrac{1}{4\,\pi^2\,f^2\,C_c^2}}{R_s} \tag{3}$$

The height of the S-shaped response curve of effective-capacity measuring instruments is determined by the value of C_c. High sensitivity of such instruments occurs in the vicinity of the inflection point of the S-shaped response curve and the most sensitive region usually covers only a ten-fold range of concentration.

At the inflection point, where the second differential, $\dfrac{d^2\,C_e}{d\,R_s^2}$ of equation (2) equals zero, $R_s = \dfrac{\sqrt{3}}{6\,\pi\,fC_c}$. (4)

Thus for instruments responding to changes in effective capacitance in the titration cell circuit, high sensitivity occurs in the range where R_s is nearly equal to $\dfrac{\sqrt{3}}{6\,\pi\,fC_c}$. At the inflection point $C_e = 3/4\,C_c$.

If log R_s is plotted against C_e, the inflection point of the curve occurs at the midpoint, the point at which $C_e = \frac{1}{2} C_c$. At this point $R_s = \frac{1}{2\pi f C_c}$. (5)

The C_e versus log R_s curve is symmetrical with respect to the point $R_s = \frac{1}{2\pi f C_c}$, $C_e = \frac{1}{2} C_c$.

The conductance loss curve has a dip at the point at which the maximum electrical energy is dissipated as heat. The minimum in the response curve, which may be obtained by equating the first differential of equation (3), $\frac{dR_e}{dR_s}$, to zero, occurs when $R_s = \frac{1}{2\pi f C_c}$. At this point, the point of minimum parallel equivalent resistance, $R_e = 2\,R_s$, and $C_e = \frac{1}{2} C_c$. (6)

Instruments measuring conductance loss changes are sensitive in the regions on either side of the minimum in the response curve. Each of these regions is wider than the sensitive region of the S-shaped response curve of instruments responsive to changes in effective capacity and thus concentration is less critical with instruments measuring conductance loss.

The relation of response curves to the physical dimensions of high-frequency cells

It can be shown that concentration limitation can be overcome by varying the physical dimensions of the high-frequency titration cells. For a cylindrical cell and sample solution with a fixed specific conductance or fixed specific volume resistivity, the equation $R_s = \varrho_s\, l/\pi\, r^2$ (7) can be applied as an approximation. Since the specific resistance (ϱ_s) and π are constant, R_s varies directly with the cell length (l) and inversely with the square of the inside radius (r^2). This formula does not take into account the fact that in the columns of the solution surrounded by the metal electrodes there are effectively an infinite number of infinitesimally small capacitors. Electrically, this is somewhat similar to the phenomenon of characteristic impedance encountered in transmission lines. However, the approximation is valid. Progressively varying the electrode separation distance, for a given cell tube and sample solution, or varying the inside diameter of the titration vessel, for a constant electrode length and electrode separation distance, shifts the useful concentration regions of the response curves.

The external electrode itself can be considered as the outer plate of a coaxial cylindrical capacitor and, neglecting fringe effects, equation (8) gives the capacitance of C_c for electrodes of equal length.

$$C_c = \frac{Kh}{4 \ln \frac{r+g}{r}} \,. \qquad (8)$$

K is the dielectric constant of the interspace, h is the length of the metal electrode, r is the inside radius of the titration tube and g is the thickness of the cell wall. The value of C_c varies directly with the length of the electrodes and inversely with the thickness of the cell wall. Increasing the length of the metal electrodes or decreasing the cell wall thickness magnifies the change in electrical properties measured and thus gives a greater rise in the response curves.

Experimental results

Studies were made of the significance of the physical dimensions of high-frequency titration cells and the results confirmed the theoretical predictions. Cells of from 3 to 65 mm outside diameter glass tubing were used. Metal bands (copper, aluminium) of from 2.5 to 12.5 cm length served as external electrodes. The electrode separation distances ranged from 1.5 to 60 cm.

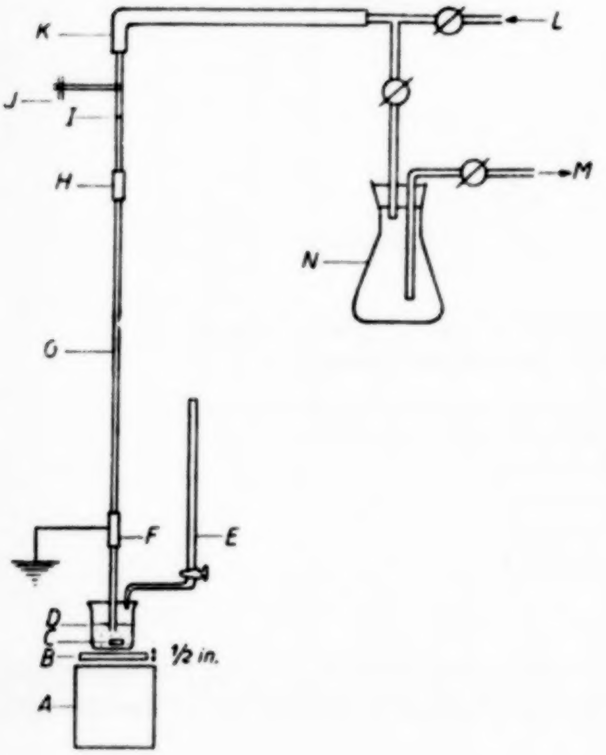

Fig. 2. High-frequency titration cell apparatus.
A. Magnetic stirrer.
B. Thermally and electrically insulating support.
C. Stirring bar.
D. 150-ml beaker.
E. Burette.
F. Grounded electrode.
G. Glass titration tube.
H. Sensitive electrode.
I. Liquid level mark.
J. Plastic clamp.
K. Neoprene tubing.
L. Air or nitrogen inlet.
M. Aspirator outlet.
N. Partially evacuated flask.

The experimental setup for the narrower cells is illustrated in Fig. 2. After each increment of titrating reagent was added to the sample, the solution was thoroughly stirred, a portion was drawn up into the glass tubing and its effective conductance or capacitance measured by

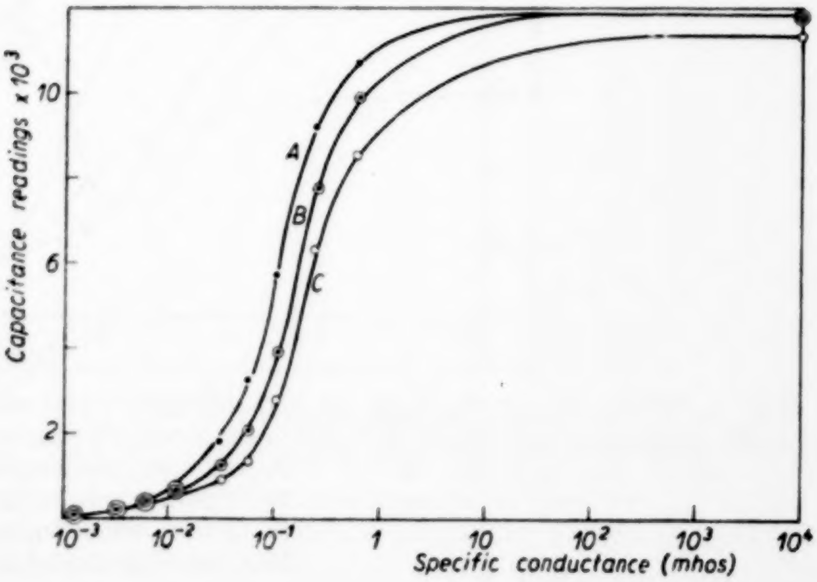

Fig. 3. Effect of electrode separation distance on high-frequency response curves.
9-mm flint glass tubing. 6.3-cm aluminium foil electrodes.
A. 30-cm electrode separation distance.
B. 46-cm electrode separation distance.
C. 61-cm electrode separation distance.

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the high-frequency method. The liquid was then returned to the bulk solution and the process repeated. The larger diameter titration cells were in the form of test tubes. Both air and magnetic stirring were employed.

The effect of varying the electrode separation distance for a glass tube of constant diameter is shown in Fig. 3. Increasing the distance between the electrodes shifts the inflection point of the curve to higher electrolyte concentrations.

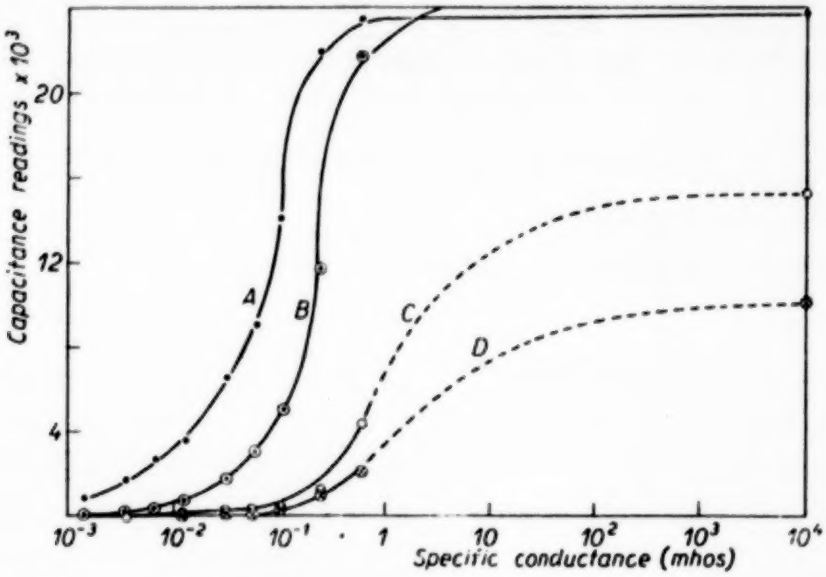

Fig. 4. Effect of cell diameter on high-frequency response curves (apparatus of Fig. 2). 30.5-cm electrode separation distance. 12.7-cm aluminium foil electrodes.

A. 13-mm glass tubing.
B. 9-mm glass tubing.
C. 4-mm glass tubing.
D. 3-mm glass tubing.

The effect of varying the diameter of the titration cell is shown in Figs. 4 and 5. Increasing the diameter of the cell shifts the inflection point of the curve to lower electrolyte concentrations.

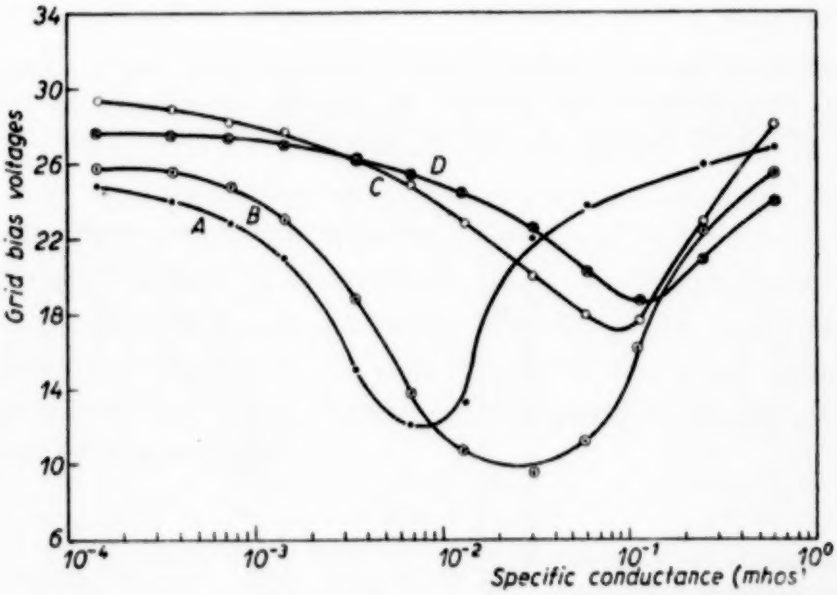

Fig. 5. Effect of cell diameter on high-frequency response curves (apparatus of Fig. 2). 3-cm aluminium foil electrodes. 30.5-cm electrode separation distance.

A. 13-mm glass tubing.
B. 9-mm glass tubing.
C. 4-mm glass tubing.
D. 3-mm glass tubing.

Table I summarizes the extremely wide concentration range that can be investigated when both the distance of separation of the electrodes and the diameter of the cell are varied. The sensitive regions of the response curves vary from specific conductances corresponding to $2 \cdot 10^{-3} N$ KCl solutions to concentrated hydrochloric acid. Figs. 6 and 7 verify the assumption that the value of C_c is related directly to the length of the electrodes and inversely to the cell wall thickness.

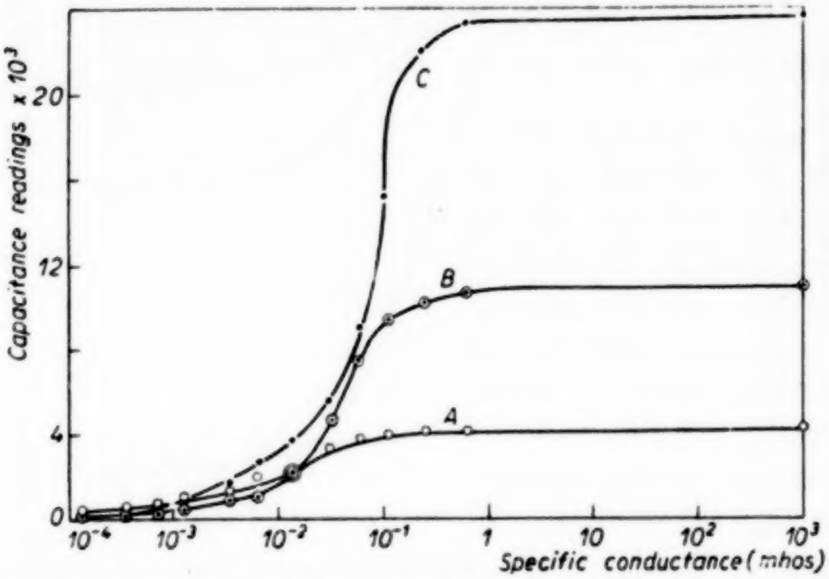

Fig. 6. Effect of electrode length on high-frequency response curves. 13-mm Pyrex glass tubing. 30.5-cm electrode separation distance.
A. 2.5-cm electrodes.
B. 6.3-cm electrodes.
C. 12.7-cm electrodes.

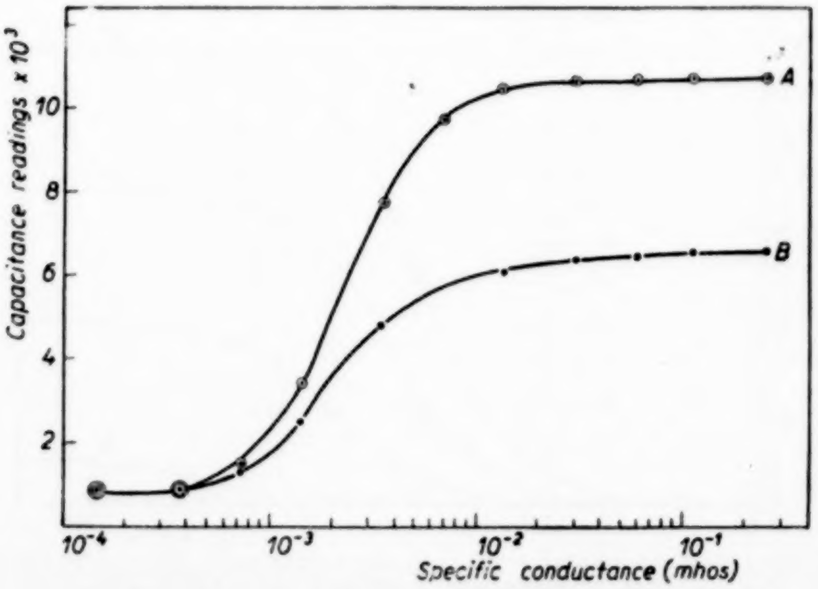

Fig. 7. Effect of wall thickness on high-frequency response curves. 29-mm O.D. Pyrex test tube cells. 3-cm aluminium foil electrodes. 10-cm electrode separation distance.
A. 2.5-mm wall thickness.
B. 3.9-mm wall thickness.

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Fig. 8 shows a family of response curves obtained with the Sargent Oscillometer connected to different mica capacitors in series with various values of non-inductive resistors. Instrument response, given in units on the Oscillometer, where each unit equals about 0.005 mmfd, is theoretically related to the capacitor and resistor values by equation (2). Theoretical response curves, calculated from equations (2) and (3) are given in Figs. 9 and 10.

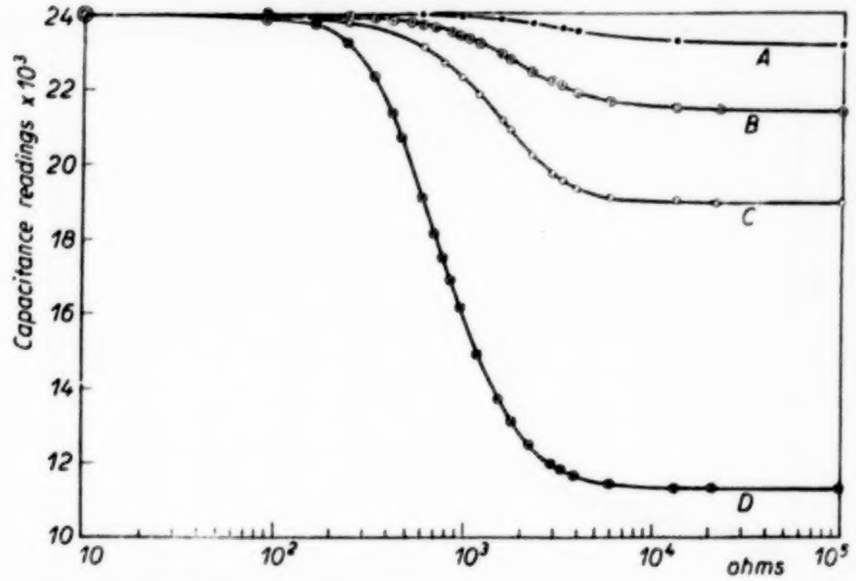

Fig. 8. Response curves for series resistance-capacitance circuits.

A. C_c = 5 mmfd
B. C_c = 12 mmfd
C. C_c = 24 mmfd
D. C_c = 50 mmfd

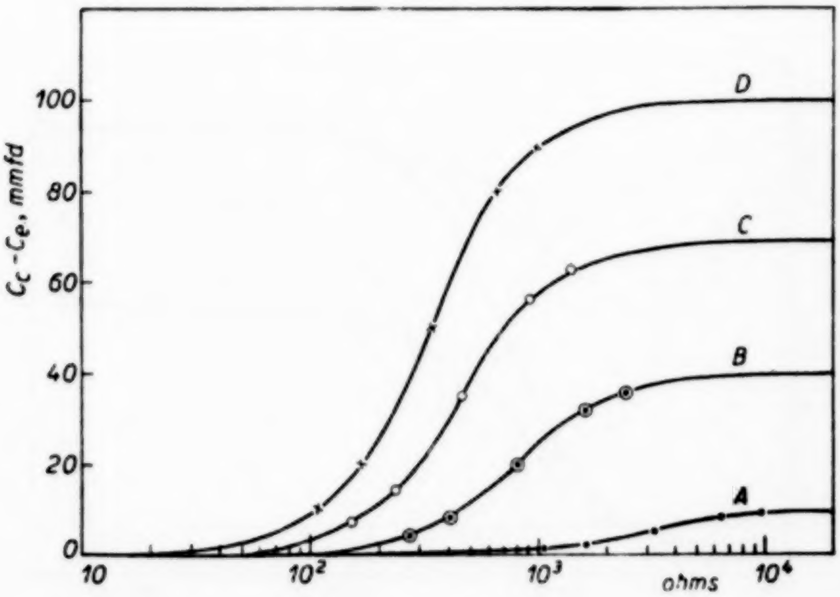

Fig. 9. Plot of equation 2, with f = $5 \cdot 10^6$ C.P.S.

A. C_c = 10 mmfd
B. C_c = 40 mmfd
C. C_c = 70 mmfd
D. C_c = 100 mmfd

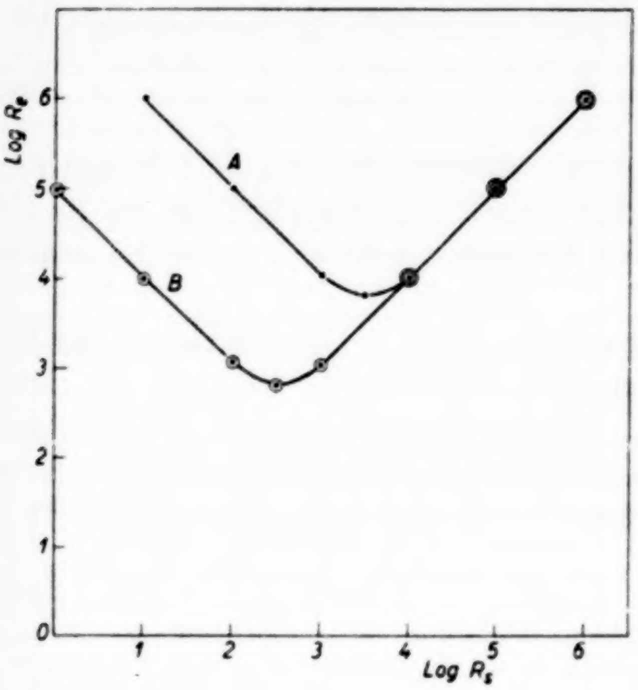

Fig. 10. Plot of equation 3, with $f = 5 \cdot 10^6$ C.P.S.
A. $C_e =$ 10 mmfd
B. $C_e =$ 100 mmfd

DISCUSSION

The families of curves in Figs. 4, 8, and 9, obtained by plotting response of the Oscillometer to a number of cylindrical high-frequency cells containing various conductive solutions, by plotting response of the Oscillometer to series resistance-capacitance circuits and by plotting the theoretical response curves show that, as an approximation for instruments which measure effective capacitance changes, a cylindrical high-frequency cell can be described in terms of the simplified series equivalent circuit of Fig. 1, B.

The families of curves in Fig. 10, obtained by plotting equation (3) and in Fig. 5, obtained by plotting the response of the conductance-loss instrument to a number of cylindrical high-frequency cells containing conductive solutions show that the same considerations hold for this type of instrument.

TABLE I

EFFECT OF TITRATION CELL DIAMETER SARGENT OSCILLOMETER

Outside cell diameter, mm	*Electrode separation distances, cm*	*Approximate effective concentration region*	
		Specific conductance (mho)	Example
3	30.5	$6 \cdot 10^{-1}$	Concentrated HCl
4	30.5	$6 \cdot 10^{-1}$	Concentrated HCl
9	30.5	$2.5 \cdot 10^{-1}$	Saturated NaCl
13	30.5	$1.1 \cdot 10^{-1}$	1.0*N* KCl
25	10.0	$4.1 \cdot 10^{-3}$	0.03*N* KCl
29	10.0	$2.8 \cdot 10^{-3}$	0.02*N* KCl
38	10.0	$1.4 \cdot 10^{-3}$	0.01*N* KCl
40	1.5	$7.2 \cdot 10^{-4}$	0.005*N* KCl
50	1.5	$5.8 \cdot 10^{-4}$	0.004*N* KCl
65	1.5	$2.9 \cdot 10^{-4}$	0.002*N* KCl

For any conductance cell the ratio of distance between electrodes to their cross-sectional area is a fixed quantity and is called the cell constant (k). Therefore, as an approximation, cylindrical high-frequency cells having electrodes at the ends may be considered to have a cell constant which relates the specific conductance of the solution in the cell to the value of R_s in the series equivalent cell circuit. The exact relationship is

$$R_s = \frac{k}{L_s} = \frac{l}{\pi\, L_s\, r^2}, \tag{9}$$

where R_s is the series equivalent resistance of the titration cell containing a solution of specific conductance L_s $(1/\varrho_s)$, k is the cell constant, l is the length of the liquid column between the electrodes of the high-frequency cell and r is the inside radius of the cylindrical cell.

Since the inflection point of the semi-logarithmic plot of ΔC_c *versus* R_s for instruments measuring effective capacitance changes occurs at the value of R_s given by equation (5), the physical dimensions of a cylindrical high frequency cell for which maximum sensitivity will be obtained with electrolytes of a given specific conductance can be determined. On substituting equations (8) and (9) in equation (5), it is found that

$$L_s = \frac{K\, f\, h\, l}{2r^2 \ln \dfrac{r+g}{r}}. \tag{10}$$

Thus, in order to design a high-frequency titration cell suitable for a given titration, the specific conductance of the solution at the end-point of the titration is determined or estimated. From this value the physical dimensions of the cell can be determined using equation (10).

Constant-temperature systems

Very accurate high-frequency measurements require some method of temperature regulation, although this is generally ignored. The conductivity of solutions is dependent on the temperature and increases rapidly with rise in temperature (2% to 2.5% per degree C for aqueous solutions). In addition the dielectric constants of liquids fall with increased temperature.

Due to its high dielectric constant water seems unsuitable as a constant temperature liquid for high-frequency measurements involving organic compounds. Moreover, contamination of aqueous systems with resulting change in conductance is difficult to avoid. However, constant-temperature systems were devised to permit both aqueous and non-aqueous liquids to be used as circulating media.

For the narrow tubing titration cell apparatus, Fig. 2, a glass beaker surrounded by a jacket through which constant-temperature liquid was pumped gave excellent temperature regulation. The beaker was lowered to remove the narrow glass tube from the bulk of the solution and the measurements were taken rapidly. Since the beaker is not electrically connected to the titrimeter cell during readings, water can be used as a constant temperature medium.

With the larger diameter test-tube titration cells satisfactory temperature regulation was obtained by making the lower electrode a hollow copper jacket or simply tightly wrapping copper tubing around the one metal foil electrode. Since this electrode was grounded, constant-temperature water could be used as the circulating liquid. For a difference of ± 3° C between room temperature and bath temperature, these devices were capable of regulating the sample temperature within ± 0.1° C. Some temperature regulation was obtained by circulating constant-temperature water through the grounded inner electrode of a Sargent Type B titration cell.

SUMMARY

The present work was undertaken to overcome the disadvantage of the limited concentration range of high-frequency measurements. Instruments which respond to either effective capacitance or effective conductance changes were used. A cell was designed to minimize the dielectric constant contribution of the solution, and respond only to conductance. Studies on the significance of the physical dimensions of high-frequency titration cells were carried out. Progressively varying the electrode separation distance or the diameter of the titration vessel shifted the useful concentration regions of the response curves. Increasing the length of the metal electrodes or decreasing the cell wall thickness magnified the response of the effective concentration regions. An equation was derived relating the specific conductance of the sample solution to the physical dimensions of the high-frequency cell necessary for maximum sensitivity. Constant-temperature systems were devised to permit both aqueous and non-aqueous liquids to be used as circulating media.

RÉSUMÉ

Ce travail a été entrepris pour pallier à l'inconvénient des limites de concentrations des mesures de haute fréquence. Des instruments répondant aux changements de capacitance effective ou de conductance effective ont été utilisés. Une cuve est proposée pour diminuer au maximum l'effet de la constante diélectrique de la solution, et répondre seulement à la conductance. Des études sur le rôle des dimensions physiques des cuves de titration à haute fréquence ont été effectuées. En faisant varier progressivement la distance entre les électrodes ou le diamètre du récipient de titration, on peut changer les limites de concentrations utilisables des courbes. En augmentant la longueur des électrodes métalliques ou en diminuant l'épaisseur des parois de la cuve, on peut étendre les limites de concentrations effectives. Une équation a été établie donnant la relation entre la conductance spécifique de la solution à analyser et les dimensions de la cuve de haute fréquence nécessaire pour un maximum de sensibilité. Des systèmes à température constante, à circulation de liquides aqueux ou non aqueux, ont été proposés.

ZUSAMMENFASSUNG

Diese Arbeit wurde unternommen, um die Schwierigkeiten zu überwinden, welche von den Konzentrationsgrenzen der Hochfrequenzmessungen herrühren. Es wurden Instrumente verwendet, welche den Änderungen der effektiven Kapazitanz und der effektiven Konduktanz angepasst sind. Es wird eine Zelle vorgeschlagen, um den Effekt der dielektrischen Konstante der Lösung am meisten zu verringern und um nur die Konduktanz allein wirken zu lassen. Es wurden Untersuchungen ausgeführt über die Rolle der physikalischen Dimensionen der Hochfrequenztitrationszelle. Indem man progressiv die Distanz zwischen den Elektroden oder den Diameter des Titrationsgefässes variiert, kann man die gebräuchlichen Konzentrationsgrenzen der Kurven ändern. Wenn man die Metallelektroden verlängert oder wenn man die Wanddicke der Zelle verringert, kann man die effektiven Konzentrationsgrenzen ausdehnen. Es wurde eine Gleichung aufgestellt, welche die Abhängigkeit gibt, zwischen der spezifischen Konduktanz der zu analysierenden Lösung und den Dimensionen der Hochfrequenzzelle, welche notwendig ist um ein Maximum an Empfindlichkeit zu erreichen. Systeme mit konstanter Temperatur, in denen wässrige oder nicht wässrige Flüssigkeiten zirkulieren können, wurden vorgeschlagen.

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HIGH FREQUENCY TITRATIONS INVOLVING CHELATION WITH ETHYLENEDIAMINETETRAACETIC ACID

V. COMPLEXATION WITH RARE EARTHS

by

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It has already been established that the rare earth metals form stable complexes with ethylenediaminetetraacetic acid. BRINTZINGER, THIELE AND MILLER obtained the complexes $LaH(C_{10}H_{12}N_2O_8)$ and $NdH(C_{10}H_{12}N_2O_8)$[1], and VICKERY[2] prepared various lanthanon group complexes and studied their absorption spectra. The formation of ethylenediaminetetraacetic acid complexes has also been utilized in the separation of rare earths[3,4,5,6]). The chemical and physical properties of ethylenediaminetetraacetic acid complexes of the rare earth metals have been studied by potentiometric and electrometric titrations, spectrophotometry, electrophoresis and other physico-chemical approaches[6,7,8].

The present investigation was undertaken to study complexation of rare earths by ethylenediaminetetraacetic acid through the use of high frequency methods and to establish the possibilities of high frequency titrations for the quantitative determinations of these metals.

EXPERIMENTAL

Chemicals. Lanthanum, cerium(III), neodymium, and praseodymium nitrates, and gadolinium bromate were used. With the exception of gadolinium bromate, these salts were of reagent grade with certified purities of 99.9%. The purity of the gadolinium was not indicated nor was the nature of impurities given. It was assumed that the principal contaminants were rare earths and, because of the nature of the studies, these would not introduce serious error. All of the rare earth solutions were standardized by precipitation of the respective rare earth oxalates with subsequent conversion and weighing as the corresponding oxides. Reagent grade ethylenediaminetetraacetic acid (Versene) and disodium ethylenediaminetetraacetate were used. Standard solutions of these reagents were checked against primary standard calcium and copper salts using high frequency titrations as described previously[9]. In the studies of the quantitative determination of the rare earths, further standardization of the disodium ethylenediaminetetraacetate was made by titration against known amounts of lanthanum.

Apparatus. A Sargent Model V Oscillometer was used for all high frequency measurements. Titrations were performed using the large cell (100 ml). Hydrogen ion concentrations were measured using a Beckman Model G pH meter.

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Determination of reacting ratios of rare earth metals to ethylenediaminetetraacetic acid

The ratio of reactants was followed by titration of the hydrogen ions released through chelation:

$$H_4Y + MX_3 \rightarrow MHY + 3H^+ + 3X^-$$

and

$$MHY \rightarrow MY^- + H^+$$

(H_4Y represents ethylenediaminetetraacetic acid, M symbolizes any rare earth metal, and X designates an anion). The liberated protons were titrated with standard base using the Oscillometer to establish the end-points. All of the rare earths yielded curves in which the amount of hydrogen ions released increased with increasing ratios of metal to addendum until 1 to 1 ratios were attained.

The experimental procedure can be illustrated by the typical case of lanthanum. One hundred milliliters of $1/3032\,M$ ethylenediaminetetraacetic acid were placed in the titration cell of the Oscillometer. Standard lanthanum nitrate was then added in increments selected to give definite metal to addendum ratios. The mixtures were stirred and the released protons were titrated with $1/90.9\,M$ sodium hydroxide. The resulting high frequency titration curves are illustrated in Fig. 1.

As shown in Fig. 1, the titration curve for the addendum alone gave an inflection point at two mole equivalents of base. With the addition of lanthanum the inflection point shifted progressively until at a 1 to 1 ratio, 4 mole equivalents of base were required. Up to this ratio, the end-points appeared as sharp reversals in the titration curves. Beyond this ratio there was no shift in the point of inflection and a pronounced alteration occurred in the shape of the curve. Excess lanthanum, beyond a 1 to 1 ratio, prevented the usual reversal of the titration curves and this may be interpreted

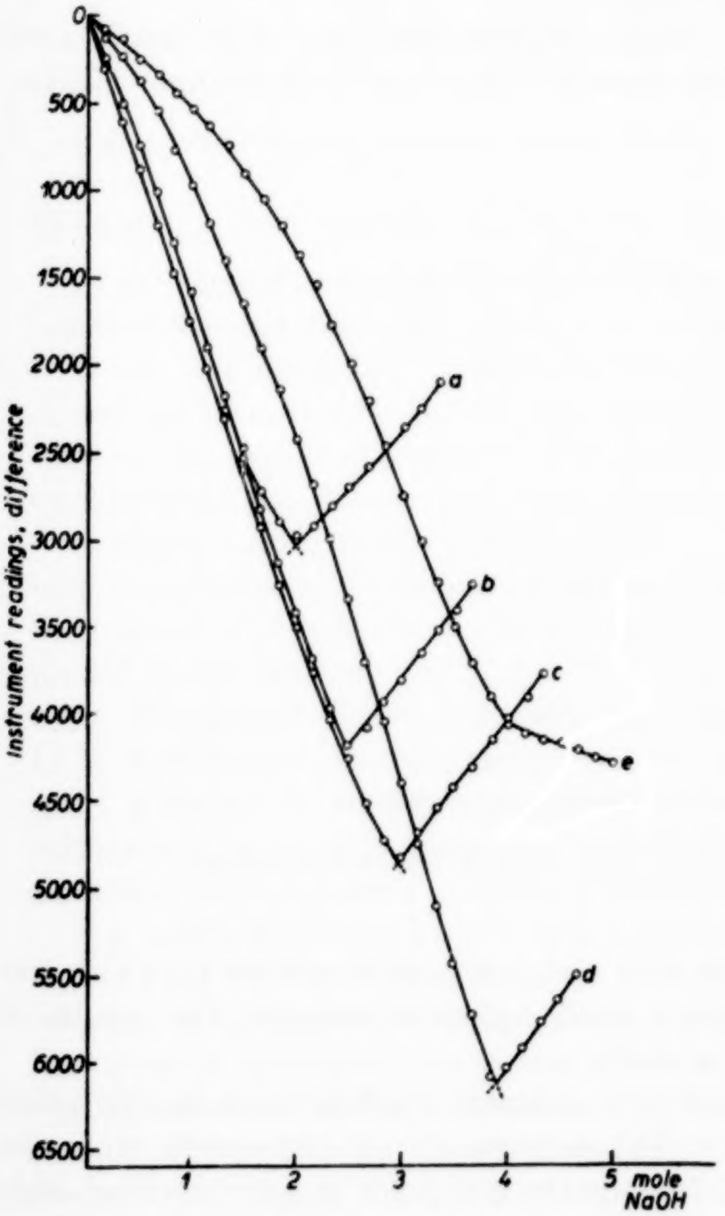

Fig. 1. Sodium hydroxide titrations of lanthanum nitrate and EDTA.

(a) Addendum only
(b) 1 : 4 (La : addendum)
(c) 1 : 2 (La : addendum)
(d) 1 : 1 (La : addendum)
(e) 2 : 1 (La : addendum)

as indicating direct reaction between sodium hydroxide and uncomplexed (excess) metal.

The position of the inflection point is determined by the amount of metal present when excess complexer is present. This stoichiometric relationship lends itself to the quantitative estimation of lanthanum and the other rare earths.

A second approach exployed for determining reacting ratios was to study simple, direct reactions between the rare earths and ethylenediaminetetraacetic acid. When a solution of a rare earth metal was added to a solution of the complexing addendum continuous complexation takes place. The course of the reaction can be followed by means of the Oscillometer and when an excess of metal ion is attained, a distinctive response is shown by the instrument. Lanthanum can again be used to illustrate the studies made of the various rare earth metals.

One hundred milliliters of 1/3000*M* ethylenediaminetetraactic acid were placed in the large cell of the Oscillometer and titrated with 1/150*M* lanthanum nitrate.

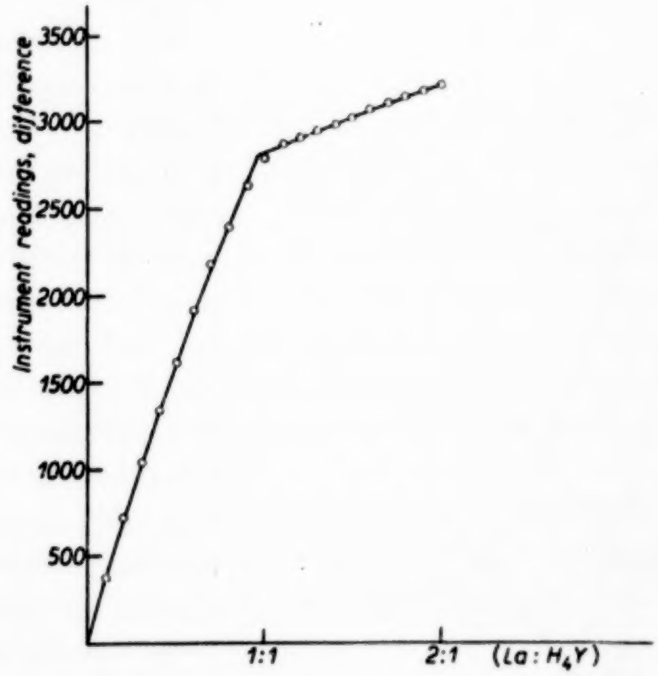

Fig. 2. Titration of 1/3000*M* EDTA with 1/150*M* lanthanum nitrate.

The titrations were made at the pH of the free acid (2.8–3.0), and at pH 10. The latter value was obtained by adjustment with 1/10*M* sodium hydroxide. The results of typical titrations are shown in Figs. 2 and 3.

The curve in Fig. 2 shows an increase in instrument reading until an end-point is obtained at reactant ratios of 1 to 1. The instrument response results from the release of protons during complexation. Beyond the end-point excess metal salt adds gradually to the Oscillometer response but the effect is much less than that given by liberated protons. The curve gives clear indication of 1 to 1 reaction ratios.

The curve shown in Fig. 3 represents a typical titration made at pH 10. In this case there is a slow decrease in instrument response until an end-point is reached at equal molar concentration of reactants. Up to this end-point the hydrogen ions being released in the reaction are removed due to the rather high alkalinity of the test medium. Beyond the end-point the titration curve drops sharply: this is probably

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due to the precipitation of the metal hydroxide. The reversal point shown at approximately 1.5 mole of titrant marks the end-point of hydrolysis and the upward break of the curve represents the simple loading effect of added electrolyte.

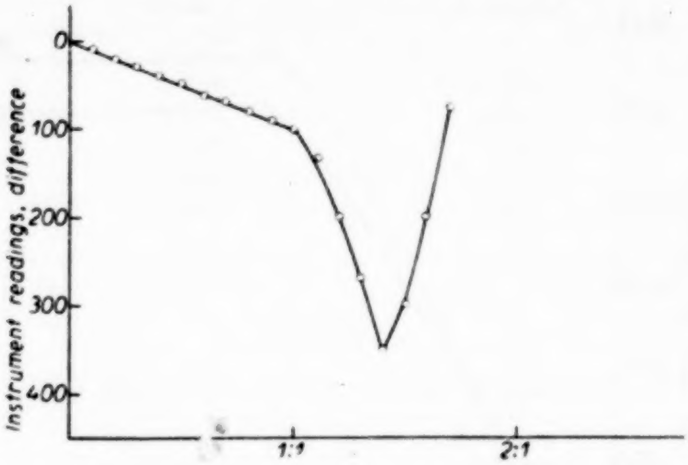

Fig. 3. Titrations of 1/1000M sodium EDTA with 1/50M lanthanum nitrate at pH 10.

Quantitative determination of rare earth metals

As mentioned in discussing the determination of reacting ratios, the hydrogen ions released through chelation of the rare earth metals and ethylenediaminetetraacetic acid are quantitatively related to the amount of metal present provided excess complexer is used. It is well known that this type of reaction can be used quantitatively by the simple expedient of titrating liberated protons with standard base. The Oscillometer can be recommended for use in such titrations.

A second quantitative technic is based on the direct titration of the rare earth metals with standard disodium ethylenediaminetetraacetate. It is to be recommended because of its simplicity. In the proposed method, 100 ml of test solution should be placed in the titration cell of the Oscillometer and titrated with the standard versenate. The titrant should preferably be standardized against pure salts of the metal to be determined. An alternate procedure is to add sodium acetate-acetic acid buffer (pH 5.3) before the titration. One ml of 1/5M buffer solution is sufficient for use with solutions of rare earths that are 1/3000M or less in strength. The use of the buffered solutions provides more distinct end-points as may be seen from Figs. 4 and 5.

The curves shown in Figs. 4 and 5 serve to illustrate the results obtained with all of the rare earths. The curves in Fig. 4 show that in unbuffered solutions an increase in instrument readings occurs up to the end-point. This effect is due to the liberation of hydrogen ions during the reaction. The characteristic curves shown in Fig. 5 indicate that the net ionic strength of the metal solution is reduced through complexation with the ethylenediaminetetraacetate. The buffer present removes the liberated protons so there is a sharp decrease in Oscillometer response as titrations progress. At the end-point an abrupt reversal occurs and further additions of titrant result in a pronounced load on the titrimeter. Continued additions of excess sodium ethylenediaminetetraacetate produce a steeply ascending curve.

Titrations in buffered solutions are quite accurate and small increments of titrant can be clearly indicated. Table I summarizes the results obtained in typical titrations conducted in buffered solutions. In all titrations, with the exception of gadolinium, errors ran under 0.5%. In the determination of gadolinium the errors were found to run over 1% but this might be associated with the impurities which were known to be present in the gadolinium salts available.

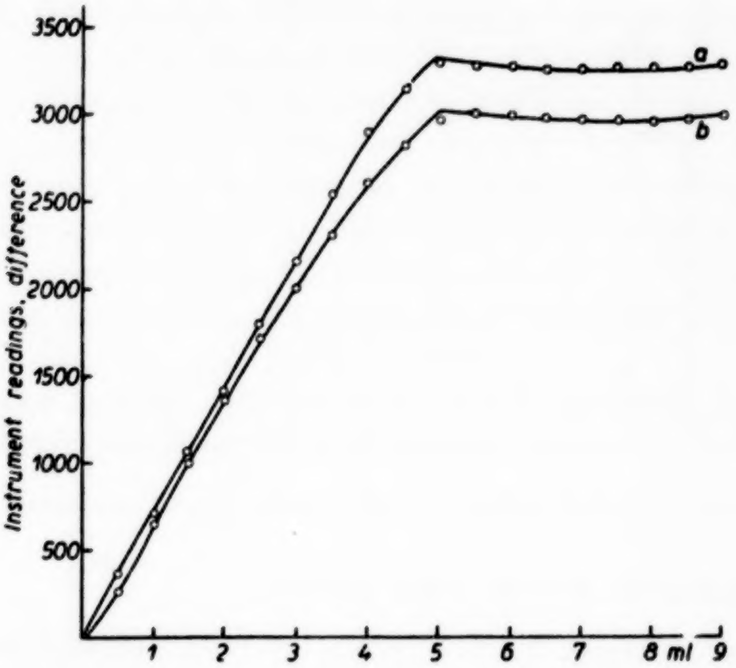

Fig. 4. Titrations of gadolinium bromate and cerous nitrate with disodium EDTA
(a) Titration of 1/3012M gadolinium bromate with 1/150M disodium EDTA.
(b) Titration of 1/3005M cerous nitrate with 1/150M disodium EDTA.

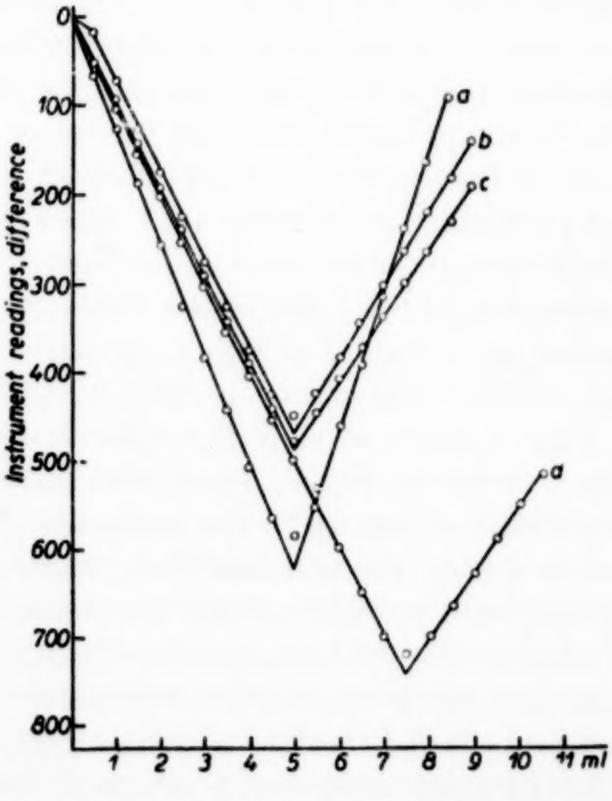

Fig. 5. Titration of cerous, praseodymium and neodymium nitrates with disodium EDTA in acetic acid sodium acetate buffer (pH 5.3).
(a) Titration of 1/3005M cerous nitrate with 1/150M disodium EDTA.
(b) Titration of 1/3010M praseodymium nitrate with 1/150M disodium EDTA in the **presence** of 8.71 mg barium nitrate.
(c) Titration of 1/5998M neodymium nitrate with 1/300M disodium EDTA.
(d) Titration of 1/4026M praseodymium nitrate with 1/300M disodium EDTA.

TABLE I

TYPICAL RESULTS OF DIRECT TITRATIONS IN BUFFERED SOLUTIONS

Rare earth taken (mg)	*Molarity of titrant*	*Rare earth found (mg)*	*Error (%)*
4.663 Ce^{+3}	1/150	4.680	0.36
4.663 Ce^{+3}	1/150	4.680	0.36
4.796 Nd	1/150	4.816	0.42
4.796 Nd	1/150	4.816	0.42
2.405 Nd	1/300	2.393	0.50

TABLE II

EFFECT OF ADDED ELECTROLYTES

Rare earth taken (mg)	*Salt added (mg)*	*Rare earth found (mg)*	*Error %*
4.663 Ce^{+3}	8.71 $Ba(NO_3)_2$	4.615	1.29
4.796 Nd	5.66 $AgNO_3$	4.765	0.65
4.796 Nd	3.70 KCl	4.776	0.42

Interferences

Oxalates must be absent but chloride, iodide, bromide, thiocyanate, bromate, sulfate and chromate can be tolerated in small amounts. Of the cations only the alkali metals, ammonium, barium, strontium, silver, and thallium(I), are without serious effect. Excess salts, regardless of their nature, must be avoided because of the "loading" effect they exert on the high frequency titrimeter. The higher the salt concentration the less sensitive is the instrument. For solutions of rare earths in the range of 1/3000*M* "indifferent" electrolytes should not total over 1/2000*M*. Table II gives some results of titrations made in the presence of diverse salts.

DISCUSSION

Ethylenediaminetetraacetic acid reacts with rare earth metals at a 1 to 1 ratio. This reaction ratio has been confirmed by high frequency titrations over the pH range of 2.8 to 10, indicating that the rare earths form stable complexes over a wide range of acidities. In this regard, the rare earth metals differ from thorium.

Quantitative titrations of rare earth metals can be made using the high frequency titrimeter for following the course of the titrations. Direct titrations with disodium ethylenediaminetetraacetate and acetic acid-sodium acetate buffered solutions give the best results.

SUMMARY

High frequency titrations have been utilized in studying the chelation of rare earth metals with ethylenediaminetetraacetic acid. The use of high frequency titrations for the determination of rare earth metals has also been studied. A procedure is proposed based on direct titrations with disodium ethylenediaminetetraacetate in buffered solutions. Excellent end-points are obtained and the method is accurate in the absence of other metals that might react with the titrant.

RÉSUMÉ

Des titrations à haute fréquence ont été utilisées pour l'étude de la formation des chélates des métaux des terres rares avec l'acide éthylènediaminotétraacétique. Ces titrations à haute fréquence ont également été étudiées en vue de leur application au dosage des métaux des terres rares. Une méthode est proposée; elle est basée sur la titration directe au moyen de l'éthylènediaminotétraacétate disodique, en solutions tampons. Des points finals excellents ont été obtenus; la méthode est précise, en l'absence de métaux pouvant réagir avec le réactif.

ZUSAMMENFASSUNG

Hochfrequenztitrationen wurden zur Untersuchung von Metallchelaten der seltenen Erden mit der Äthylendiaminotetraessigsäure angewandt. Die Verwendung der Hochfrequenztitrationen für die Bestimmung der Metalle der seltenen Erden wurde gleichfalls untersucht. Es wird eine Methode vorgeschlagen, welche auf der direkten Titration mit Hilfe von Dinatriumäthylendiaminoacetat, in Pufferlösungen, basiert. Es wurden hervorragende Endpunkte erhalten. Die Methode ist präzis, falls keine Metalle vorhanden sind, die mit dem Reagenz reagieren können.

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INVERSE POLAROGRAPHY WITH STATIONARY AMALGAM ANODES
I. BASIC PRINCIPLES AND TECHNIQUE

by

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INTRODUCTION

A recent comprehensive investigation[1] of the anodic dissolution of stationary amalgam anodes has shown that the rate-determining factor is the diffusion of the metal in mercury up to the amalgam/electrolyte interface. When the potential of such an amalgam electrode is made progressively less negative, the metal begins to ionize and dissolve close to its reversible potential and the current rises to a limiting value which cannot be exceeded until some new dissolution process sets in. The limiting current density is very steady and reproducible, it is independent of the dissolution medium, it is only very slightly dependent upon temperature, and it is simply related to the concentration of the amalgam. Furthermore the limiting current is not complicated by the presence of any residual or migration currents, and its actual value can be made large by increasing the area of the amalgam anode. It is at once apparent that such metal diffusion currents may have important analytical applications, and in the present work an attempt has been made to utilize them for the detection, separation and estimation of the heavy metals which are soluble in mercury. The proposed method involves two main operations:

(1) The metal ions present in an aqueous solution are electrolytically deposited in a mercury cathode. In this way they can be separated completely from acid radicals and organic material, and owing to the "gathering" power of the mercury cathode the metal ions from a large volume of very dilute solution can be collected.

(2) The amalgam electrode formed in (1) is then washed and combined with a suitable reference electrode in an inert aqueous dissolution medium and the cell thus formed is allowed to supply current against an opposing voltage set up on a potentiometer. By decreasing the potentiometer voltage in stages and reading the current from a microammeter a discharge curve can readily be constructed in which each metal gives rise to a sharply defined wave which serves both to characterize it and to indicate its concentration in the amalgam.

CONDITIONS FOR QUANTITATIVE DEPOSITION OF METAL IONS

The rate at which metal ions can be discharged from an aqueous solution into a stationary mercury cathode is governed by the rate of convective diffusion of the ions in the aqueous medium to the electrode surface. If the ions are discharged in electrolysis at the limiting rate, then straightforward application of diffusion layer theory leads to the relation

$$C = C_0 \cdot e^{-\frac{AD.t}{Vs}} \tag{1}$$

where C_0 is the initial concentration of the ions in g ion/ml, and C is the concentration after deposition for t seconds from V ml of solution into a cathode of area A sq.cm, D being the diffusion coefficient (cm^2 sec^{-1}) of the metallic ions and s the thickness of the diffusion layer in cm. This relation can be written as

$$t = \frac{2.303\ Vs}{AD} \log \frac{C_0}{C} \tag{2}$$

which predicts that the time required for the deposition of a given fraction of the metallic ions present is

(i) independent of the initial concentration;
(ii) directly proportional to the electrolyte volume;
(iii) inversely proportional to the area of the cathode.

In terms of current, this equation becomes

$$t = \frac{2.303\ Vs}{AD} \log \frac{I_0}{I} \tag{3}$$

where I_0 is the initial limiting current and I that after time t.

Equation (3) was verified by LINGANE[2] for deposition of metallic ions from stirred solutions under conditions such that s is constant. In unstirred solutions the position is rather more complicated since the thickness of the diffusion layer tends to change slightly with variation of concentration, but a very full investigation has been made in the present work using thallium as test metal and depositing it under controlled potential conditions. The results show that provided allowance is made for variations in s (which can be done by using data from current/potential curves) equations (2) and (3) hold quite accurately and the predictions made have been verified.

To make a further test of the time-concentration equation (2) under less idealized conditions, a series of experiments was conducted in which the current was fixed at an arbitrary high value in excess of the limiting current for metal deposition so that hydrogen was freely and continuously evolved at the mercury cathode. Under these conditions stirring by hydrogen bubbles was found very greatly to increase the rate of metal deposition; the effect was considerably greater than that ordinarily produced by mechanical agitation of the solution. The gas stirring increased with rise of current density of hydrogen evolution but appeared to approach a constant maximum value when hydrogen was being evolved at current densities greater than 0.1 A/sq.cm. Under such conditions of constant gas stirring, equation (2) appeared to hold satisfactorily. The corresponding limiting thickness of diffusion layer s was *ca.* 0.0004 cm at 20° C as compared with values of 0.01-0.03 cm for unstirred solutions. Using the value $s = 0.0004$ cm and taking $D \approx 10^{-5}$, equation (2) may be written

$$t\ (\text{min}) \approx 1.5\ \frac{V}{A}\ \log \frac{C_0}{C} \qquad (4)$$

Thus for 1 ml of solution electrolysed with a 1 sq.cm mercury cathode under conditions of vigorous hydrogen evolution the time taken for a tenfold change in concentration of the metallic ion which is deposited should be approximately 1.5 min and more than 99.9% of the metallic ion should be removed from solution in a 5 min electrolysis.

This result was used as a guide in selecting conditions for satisfactory quantitative deposition of metallic ions. It was decided in general to use 1 ml of solution rendered highly conducting by addition of sulphuric or nitric acid and to electrolyse with a 1 sq.cm mercury cathode at 0.1 A current for 10 min. Numerous tests showed that under these conditions satisfactory quantitative deposition of heavy metallic ions at any initial concentration not greater than 0.1M could readily be achieved.

APPARATUS AND TECHNIQUE

The general apparatus and circuit arrangement adopted is shown in Fig. 1. 1 ml of mercury, measured from a small burette, is taken in a glass cup electrode (cross sectional area *ca.* 1 sq. cm) provided with sealed-in platinum contact and 1 ml of the acidified solution for analysis is pipetted on to it. A small platinum rod anode is introduced into the solution which is electrolysed at 0.1 A for 10 min. The anode is then withdrawn, the electrolyte washed out with water, the amalgam stirred with a small glass ring stirrer, and the cup is then ready for use as an amalgam anode. For this purpose it is necessary to combine it with a large unpolarizable reference electrode of low resistance in a suitable dissolution medium. It has been found that a very suitable reference electrode consists of mercury in contact with excess mercurous sulphate in saturated potassium sulphate solution. This may be conveniently set up and used repeatedly by placing the mixture in the lower part of a sintered glass funnel; a fresh portion of dissolution medium is then placed above the sintered glass diaphragm for each experiment and the cup anode immersed directly in it. Saturated potassium sulphate has been most frequently used as dissolution medium, although potassium nitrate has been employed in some cases where the metallic sulphate formed by dissolution was sparingly soluble. The measured potential of the reference electrode on the hydrogen scale at 18° C is + 0.66 V, and using the arrangement described with a funnel of about 5 cm diameter and 7 cm deep the internal resistance can be kept below 30 Ω.

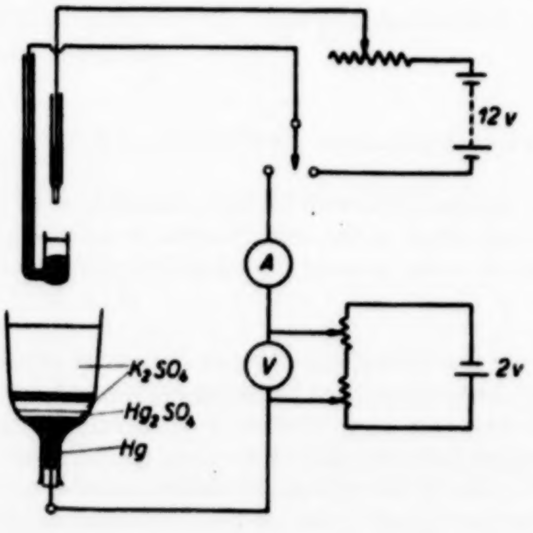

Fig. 1. Apparatus and circuit.

The voltage between the amalgam and reference electrode is opposed by a small potentiometer-voltmeter unit. This is initially set so that the potential of the amalgam is strongly negative and no current flows. The potentiometer voltage is then reduced in stages and the current passing at each setting of the potentiometer is read off from the milliammeter A which has ranges of 100 μA, 1 mA, and 10 mA severally. When a metal in the amalgam first begins to dissolve there is usually a surge of current, but this falls rapidly to a steady value as the diffusion layer is set up in the mercury surface and no difficulty is experienced in obtaining a steady current reading. Very occasionally maxima similar to those observed in polarography are apparent at the beginning of the limiting current stage but the presence of 0.01% gelatin in the dissolution medium suppresses them and improves the steadiness of the limiting currents, and this addition has generally been made. If the current is held at its limiting value for several minutes then it may fall owing to diminution in the concentration of the amalgam, but no difficulty is normally experienced in adjusting the period of observations so as to avoid errors due to this effect.

RESULTS

Typical curves

In Fig. 2 are shown typical curves for a number of common metals at different concentrations. The amount of metal indicated in each case was that present in 1 ml of the original aqueous solution; this amount was transferred to the 1 ml of mercury in the preliminary electrolysis and the curve is that for the anodic dissolution of the amalgam formed. It may be noted that each curve rises sharply from the potential axis and the initial dissolution potential seems to characterize the metal present. The current rises steeply to the limiting value and then generally remains very steady until the potential of the amalgam approaches that of the reference electrode when mercury passes into solution; the potentiometer voltage is then zero and the amalgam potential is + 0.66 V on the hydrogen scale. Using a milliammeter with the ranges specified (100 μA to 10 mA) limiting currents corresponding to 10^{-6} to 10^{-4} eqt. of most metals could be accurately measured.

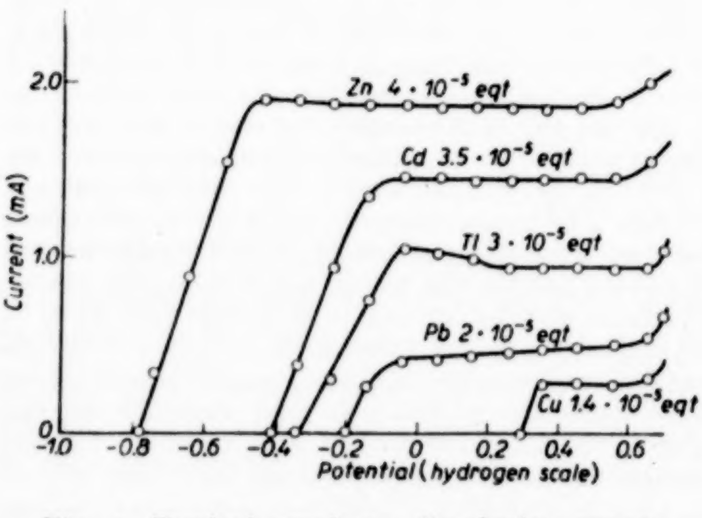

Fig. 2. Typical amalgam dissolution curves.

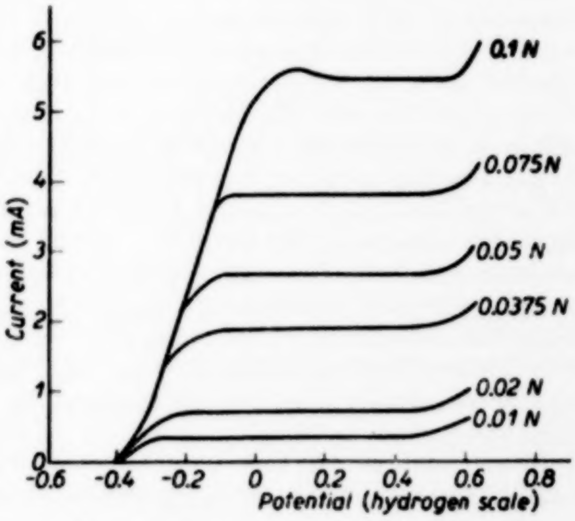

Fig. 3. Current-potential curves at different cadmium ion concentrations.

Reproducibility and concentration dependence of limiting current

In Table I is shown a set of results obtained for the dissolution of cadmium in amounts varying from 10^{-4} to 10^{-6} eqt., the concentration of the initial aqueous solution which contained 0.1 *N*-H_2SO_4 being varied from 0.1 to 0.001 *N* with respect to cadmium sulphate; some of the corresponding curves are plotted in Fig. 3.

It is at once apparent that it is the initial dissolution potential rather than the half wave potential which characterizes the metal. The relation of limiting current to concentration is shown in Fig. 4. Over any small range of concentration the relation is approximately linear, but over wide ranges of concentration it is more accurately expressed as $I = k\,C^{1.25}$ and this relation has been shown to apply fairly generally[1]. To check the reproducibility of the starting potential and limiting current value, seven separate experiments were carried out analysing 1 ml portions of 0.01 *N*-$CdSO_4$ in 0.1 *N*-H_2SO_4. The results are summarized in Table II and it can be seen that both the initial dissolution potential and the limiting current are remarkably steady.

TABLE I

ANODIC DISSOLUTION OF CADMIUM

Concn. $CdSO_4$ in aq. soln.	*Amt. of metal transferred*	*Initial diss. potl.*	*Half wave potl.*	*Limiting current*
0.1 *N*	$100 \cdot 10^{-6}$eqt.	−0.41 V	−0.19 V	5.50 mA
0.075	75	−0.41	−0.25	3.80
0.05	50	−0.41	−0.28	2.70
0.0375	37.5	−0.41	−0.33	1.90
0.02	20	−0.41	−0.31	0.73
0.01	10	−0.41	−0.34	0.37
0.005	5	−0.41	−0.35	0.175
0.002	2	−0.39	−0.33	0.057
0.001	1	−0.39	−0.32	0.017

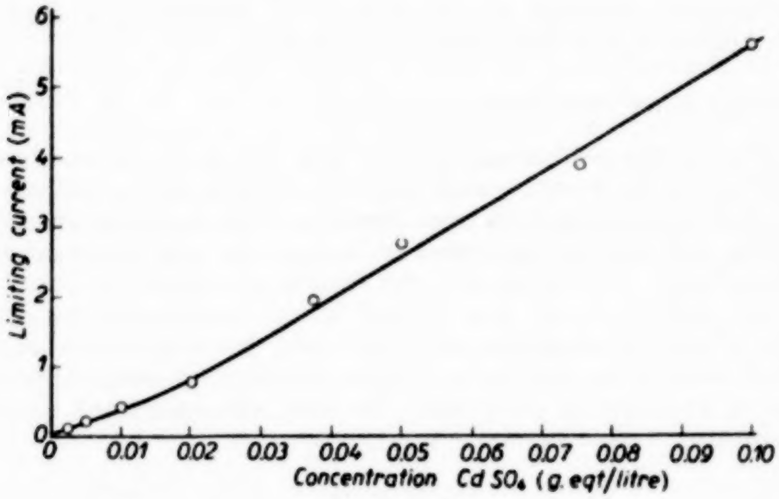

Fig. 4. Dependence of limiting dissolution currents on initial cadmium ion concentration.

TABLE II

REPRODUCIBILITY IN ANODIC DISSOLUTION OF CADMIUM (10^{-5} eqt.)

No. of expt.	*Initial diss. potl.*	*Limiting current*
1	−0.41 V	0.37 mA
2	−0.41	0.365
3	−0.41	0.37
4	−0.41	0.37
5	−0.41	0.37
6	−0.41	0.385
7	−0.41	0.365

To see what influence the period of initial electrolysis at 0.1 A had, separate experiments were carried out using 1 ml of 0.01 *N*-$CdSO_4$ in which periods of 10, 5, 4, and 3 min electrolysis were employed. Only in the last case did the limiting current show any falling off confirming that the usual period of 10 min is more than adequate.

To find what effect temperature variation would have upon the limiting current of dissolution experiments were carried out at temperatures ranging from 0 to 54° C and the results are summarized in Table III.

TABLE III

INFLUENCE OF TEMPERATURE ON ANODIC DISSOLUTION OF CADMIUM (10^{-5}eqt.)

Temperature °C	0	17	34	54
Limiting current mA	0.36	0.37	0.43	0.47

It is apparent that any normal variation of room temperature will have very little influence on the magnitude of the limiting current observed.

It might be expected that any factor influencing the area of the interface between the amalgam anode and the dissolution medium would change the limiting current, and some irreproducibility in the value might arise from variable penetration of the electrolyte between the mercury and the sides of the glass cup. That this effect does exist was shown by introducing various amounts of glass wool into the mercury surface when the limiting current was appreciably increased. Under ordinary conditions, however, the effective anodic area seems to remain very reasonably constant in different experiments. Addition of capillary active substances such as teepol to the dissolution medium at concentrations of 0.01 and 0.1% did not affect the magnitude of the limiting current substantially although the flatness of the wave deteriorated somewhat, and the presence of such substances should generally be avoided.

Collection of metallic ions from very dilute solutions

By increasing the time of the preliminary electrolysis a larger volume of aqueous sample may be estimated. Thus metallic ions in extremely dilute solutions can be gathered into the mercury electrode which will subsequently give a substantial anodic limiting current. To demonstrate this, samples containing 10^{-5} eqt. of cadmium in 1, 10, 100, and 1000 ml of solution severally were analysed by the present technique and the results are given in Table IV. For the larger volumes of solution the cup electrode was placed at the bottom of the solution contained in a tall beaker and the platinum electrode near the top; the deposition current was increased to 0.2 A to produce bulk stirring by the gas evolution. Taking the essential period for quantitative deposition from 1 ml of solution to be 5 min, the time was increased proportionately for the larger volumes of solution.

TABLE IV

ESTIMATION OF CADMIUM FROM VARIOUS SAMPLES (10^{-5} eqt.)

Sample *Vol.*	*Concn*	*Time of electrolysis*	*Initial diss. potl.*	*Limiting current*
1 ml	$10^{-2}N$-$CdSO_4$	5 min	−0.41 V	0.37 mA
10	10^{-3}	50	−0.41	0.37
100	10^{-4}	500	−0.41	0.37
1000	10^{-5}	5000	−0.41	0.37

It is seen that the cadmium has been quantitatively recovered from all solutions and gives the same limiting dissolution current. In a further of experiments using 10^{-6} eqt. cadmium the metal was quantitatively recovered from 1000 ml of $10^{-6}N$-$CdSO_4$ in $0.1N$-H_2SO_4 by electrolysis for *ca.* 5 days to give the usual anodic dissolution current of 0.017 mA.

Mixed amalgams

The conclusions drawn from the results which have been described in detail for cadmium apply equally well to manganese, zinc, lead, thallium, and copper all of which give good anodic dissolution waves. Under the deposition conditions specified from an acid medium the alkali and alkaline earth metals do not form stable amalgams and are not detected in the anodic dissolution; likewise metals such as nickel, iron and chromium which are practically insoluble in mercury fail to give anodic waves.

When mixtures of metallic ions are used the characteristic anodic wave of each metal shows up in the dissolution curve. Thus in Fig. 5 is shown the curve for a mixture of 10^{-5} eqt. each of zinc and cadmium, while in Fig. 6 the graph corresponding to $2.5 \cdot 10^{-5}$ eqt. each of zinc and thallium is given. The limiting currents to be expected from the behaviour of the metals separately

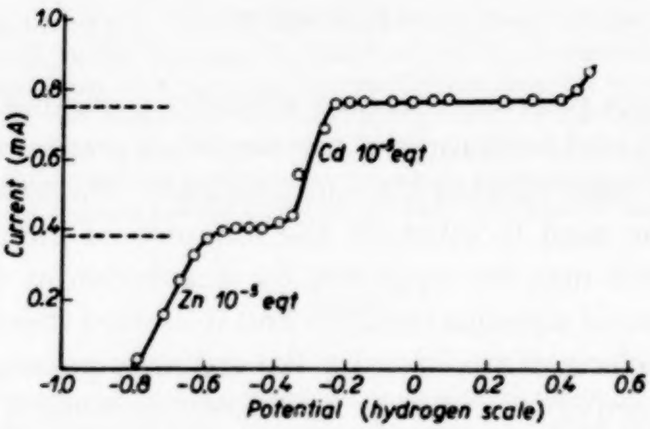

Fig. 5. Dissolution curve for mixture of zinc and cadmium.

are indicated by the dotted lines to the left of the diagrams. It is noteworthy that the first metal to dissolve from the amalgam gives its expected limiting current quite accurately and this has been generally confirmed. Subsequent limiting currents, however, sometimes tend to be higher than those expected from the behaviour of the metals singly. This effect, which has also been noted with dropping amalgam anodes[3], appears to arise by a simple electrochemical displacement reaction. When a second metal such as thallium enters the solution while the amalgam still contains a more reactive metal such as zinc, the displacement reaction $2\ Tl^{+} + Zn = 2\ Tl + Zn^{+2}$ may occur raising the surface concentration of thallium and exalting its limiting current. The effect can be minimized by avoiding any accumulation of dissolved metal ions near the amalgam surface, but it is difficult to eliminate it entirely, and it constitutes a limitation on the inverse polarographic method of analysis as applied to mixtures of metallic ions.

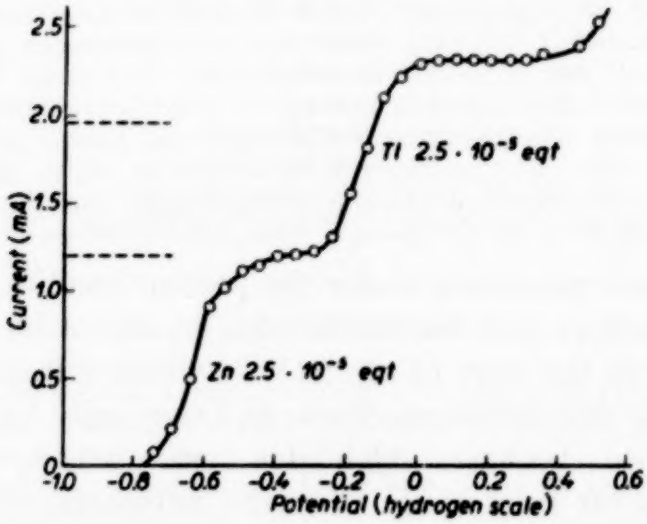

Fig. 6. Dissolution curve for mixture of zinc and thallium.

Calibration

For the estimation of any particular metal it is most satisfactory to obtain a series of limiting anodic dissolution currents with known amounts of the metal present using the cup electrode which is to be subsequently employed. With suitable calibration values obtained in this way an unknown amount of a single metal greater than *ca.* 10^{-6} eqt. can then be determined with an accuracy of about ± 1%. No attempt has so far been made to push the method to its extreme limit, although it is obvious that by increasing the sensitivity of the current measuring device much smaller quantities of metal could be estimated.

By utilizing coulometric aspects of the anodic dissolution process the necessity of calibration can be avoided although with some loss of accuracy and convenience. Thus if the potentiometer voltage is fixed at such a value that one metal only can go into solution, a graph of limiting current against time can be constructed for the duration of the dissolution process. Graphical integration then gives the quantity of electricity corresponding to the metal which has dissolved. This method is rather time consuming (1-2 hours) and the results tend to be low (within *ca.* − 5%). The period may be reduced by various devices such as measuring the quantity of electricity which passes while a known fraction of the metal dissolves as indicated by the limiting current, but again the accuracy attained is not better than about − 5%.

DISCUSSION

The present technique provides a means whereby a number of heavy metals may be quantitatively extracted from aqueous solution when present in minute amounts and at high dilutions and concentrated into an amalgam. The anodic dissolution of the amalgam may then be used to estimate the amounts of metal present directly, or alternatively the metals may be separated by dissolution at appropriate potentials into successive portions of aqueous medium and if desired these can then be analysed by other means, *e.g.* colorimetrically or by the ordinary polarographic method. Thus the technique can be employed either as a complete analytical method or as a useful preliminary operation of concentrating and separating metallic ions prior to analysis by other means.

In the anodic dissolution of metallic amalgams by the present method the initial dissolution potentials are sharply defined and seem to be fairly constant under different experimental conditions. The values are usually quite close to the standard potentials of the metals, as the following figures show, and they serve as an adequate means of characterization.

Metal	*Initial dissolution potential*	*Standard potential*
Cu	+0.30 V	+0.34 V
Pb	−0.15	−0.12
Tl	−0.26	−0.33
Cd	−0.41	−0.40
Zn	−0.78	−0.76
Mn	−1.12	−1.05

The anodic half-wave potentials under the present condition are more dependent upon experimental factors and less useful as a means of identification. Thus they may vary according to the time of electrolysis which influences the concentration of metallic ions in the dissolution medium, and they may be markedly displaced if the circuit resistance becomes high for any reason.

No attempt has so far been made to secure automatic recording of the anodic dissolution waves since one advantage of the method as described is the very simple apparatus which is required. There would appear, however, to be no great difficulty in adapting the ordinary type of recording polarograph for use with stationary amalgam anodes, and this is at present under investigation. Previous attempts to use amalgam anodes for analytical purposes have generally employed dropping amalgam electrodes and have not led to any conspicuously successful application. In the present work it is the particular features of a stationary mercury pool electrode in first serving as a cathode for the collection of metallic ions and subsequently as a large anode for metal dissolution at substantial currents which permit of useful analytical employment.

SUMMARY

A new method of electrochemical analysis has been devised in which the metallic ions present in an electrolyte are discharged into a mercury cathode. The amalgam electrode so formed is then combined with a standard reference electrode in a suitable dissolution medium and the cell thus produced is allowed to supply current against an opposing voltage set up on a potentiometer. By decreasing the potentiometer voltage in stages a curve of current against potential can be constructed for the dissolution of the amalgam anode; in this curve each metal gives rise to a characteristic wave from the height of which the amount of metal originally present can be derived. Although the method is not so universally applicable as the conventional polarographic technique with the dropping mercury cathode, it possesses advantages in sensitivity and simplicity in suitable cases and may form a useful complementary method of analysis.

RÉSUMÉ

Un nouvelle méthode électrochimique est proposée; les ions métalliques présents dans un électrolyte sont déchargés dans une cathode de mercure. L'électrode amalgamée ainsi formée est ensuite reliée à une électrode étalon de référence dans un milieu convenable; l'on fait fournir du courant à la pile ainsi obtenue en sens opposé à une tension appliquée à un potentiomètre. En diminuant le voltage du potentiomètre graduellement, une courbe de courant en fonction du potentiel peut être construite, pour la dissolution de l'anode amalgamée. Dans cette courbe, chaque métal donne une onde caractéristique, dont la hauteur permet de déterminer la teneur en métal présent. Bien que cette méthode ne soit pas aussi généralement applicable, que la technique polarographique usuelle avec la cathode à gouttes de mercure, elle présente des avantages de sensibilité et de simplicité dans certains cas; elle peut constituer une méthode d'analyse complémentaire utile.

ZUSAMMENFASSUNG

Es wird eine neue elektrochemische Methode vorgeschlagen; die in einem Elektrolyt vorhandenen Metallionen werden an einer Quecksilberelektrode entladen. Die so gebildete Amalgamelektrode wird darauf mit einer Vergleichselektrode in einem entsprechenden Medium verbunden. Man lässt dann das so entstandene Element einen Strom liefern, der einer auf ein Potentiometer angewandten Spannung entgegengesetzt ist. Wenn man die Voltspannung des Potentiometers stufenweise vermindert, kann eine Stromkurve in Funktion des Potentials für die Auflösung der Amalgamanode konstruiert werden. In dieser Kurve gibt jedes Metall eine charakteristische Welle, deren Höhe den Gehalt an ursprünglich vorhandenem Metall zu bestimmen erlaubt. Obwohl diese Methode nicht so allgemein anwendbar ist, wie die gewöhnliche polarographische Technik mit der Quecksilbertropfkathode, weist sie doch in gewissen Fällen Vorteile in Bezug auf Empfindlichkeit und Einfachheit auf. Sie kann eine nützliche Ergänzungsanalysemethode sein.

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Analysis of Insecticides and Acaricides, by F. A. Gunther and R. C. Blinn, Interscience Publishers, Inc., New York and London, 1955. viii + 696 pp., 71 fig.; price £ 5. 12.

The rapidly increasing use of insecticides, many of which are extremely toxic to human beings, has created a demand for the analysis of the insecticides themselves, and of the edible fruit or vegetables to which they have been applied. As far as the reviewer is aware, this is the first book which covers existing knowledge in this field, and it fulfils its purpose admirably. The authors have obviously drawn freely on their experience from 12 years of research activity in the analysis of insecticides and their residues on plants.

The book constitutes Vol. VI in a series of monographs on analytical chemistry and its applications, edited by B. L. Clarke and I. M. Kolthoff. It is divided into three sections: the first is a detailed discussion of the problems involved in securing quantitative data on insecticide residues on fruits and foliage, such as sampling considerations, sample processing, preanalysis or clean-up treatment, the analysis, interpretation of data, expression of results and health hazards (161 pages). Section 2 (8 pages) gives some general notes on the composition analysis of technical products. Section 3 has some 40 pages giving detailed general instructions for field sampling, measurement of samples, processing and clean-up procedures (for isolating the insecticide residues from interfering substances). These are followed by 450 pages giving in detail analytical procedures for some 90 individual insecticides and acaricides, together with a general section on determination of organic phosphorus. In general, methods are given both for composition analysis and residue analysis. The authors have drawn their methods from a wide field (almost entirely American), which includes manufacturers such as American Cyanamide, Dow Chemical, Geigy and Shell Development, and the State of California Dept. of Agriculture. All modern resources, such as infra-red spectroscopy and chromatography, are freely used. There are appendices giving detailed ultra-violet and infra-red spectra for a number of purified insecticides and acaricides and some possible accessory substances.

N. Strafford (Manchester)

BUCHBESPRECHUNG

Qualitative chemische Analyse, von Authenrieth-Rosenmund, 4. völlig umgearbeitete Auflage von Prof. Dr. K. W. Rosenmund, Verlag Th. Steinkopff, Dresden und Leipzig, 1955, viii und 152 S., 11 Abb.; brosch: Schw. Fr. 9.30, geb.: Schw. Fr. 10.35.

Für die allgemeine Beliebtheit von Authenrieth-Rosenmunds *Qualitative chemische Analyse* spricht der Umstand, dass bereits wieder eine Neuauflage und zwar die vierte notwendig geworden ist. Diese Neuauflage stellt eine wesentliche Erweiterung und auch Verbesserung dar. Besonders begrüssenswert ist, dass nunmehr auch moderne Analysenmethoden mehr als bisher Berücksichtigung fanden. So sind neben der bekannten Ammon-Sulfid-Fällung auch die Hydrolysentrennung mittels Hexamethylentetrammin und dessen Vorteile beschrieben. Der I. Abschnitt bringt die für das analytische Arbeiten und für das Verständnis der Vorgänge notwendigen theoretischen Grundlagen: Ionenlehre, elektrolytische Dissoziation, Hydrolyse, chemisches Gleichgewicht, Löslichkeitsprodukt, Spannungsreihe, pH-Definition, Pufferlösungen, Komplexverbindungen, die zweckmässig in knapper Form gehalten sind, sodass eine Überlastung des Anfängers dadurch vermieden wird. Aus dem gleichen Grunde und um dem Anfänger die Übersicht zu erleichtern, sind die sogenannten selteneren Elemente (Rb, Cs, Au, Be, Ce, Ti, Zr, Th, V, Se, Te, Mo, W, U, Pt) am Schluss des Buches im IV. Abschnitt behandelt. Der Zweck, sowohl eine Anleitung für den Anfänger als auch eine Hilfe für den Anspruchsvolleren zu bieten, erscheint durch diese Einteilung in befriedigender Weise erreicht zu sein. Im II. Abschnitt sind die wichtigsten Nachweisreaktionen der Kationen (Na, K, Li, NH_4, Mg, Ca, Sr, Ba, Al, Cr, Fe, Zn, Mn, Ni, Co, Hg, Cu, Pb, Bi, Cd, As, Sb, Sn, Ag, Tl) und Anionen in der bekannten klassischen Gruppeneinteilung beschrieben. Der III. Abschnitt ist der für den Anfänger besonders wichtigen Beschreibung des Analysenganges gewidmet: Vorproben, Analyse auf trockenem und nassem Wege, einschliesslich des in Tabellenform gebrachten Trennungsganges der Kationen und des Nachweises der Anionen. Im V. Abschnitt sind die in diesem Buch verwendeten organischen Nachweisreagenzien zusammengestellt. In diesem Zusammenhang ist es zu begrüssen, dass in der vorliegenden Auflage von den organischen Reagenzien vermehrter Gebrauch gemacht wird und auch die mikrochemischen Nachweismethoden eine stärkere Berücksichtigung finden. Auf jeden Fall kann dem Anfänger aber auch dem Fortgeschrittenen dieses Buch sehr empfohlen werden, da es einen sehr schönen Überblick über die gebräuchlichen qualitativen Methoden gibt.

G. Gorbach (Graz)

CHLOROMETHYLATION OF 8-HYDROXYQUINOLINE

by

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Several workers have reported that formaldehyde reacts with 8-hydroxyquinoline in the presence of alkali, sulphuric acid or hydrochloric acid, and that the products obtained were carbinols or diquinolylmethanes[1-6]. A Swiss patent[7] describes the preparation of a derivative of 8-hydroxyquinoline by saturating a mixture of formaldehyde and 8-hydroxyquinoline in hydrochloric acid solution, with hydrochloric acid gas. The conditions employed in this preparation are however the same as those used in chloromethylation reactions. The reaction between 8-hydroxyquinoline and formaldehyde in hydrochloric acid solution was therefore investigated in order to discover the reaction products formed under particular conditions, and to study the chelating properties of the substituted 8-hydroxyquinoline.

EXPERIMENTAL

Preparation of 7-chloromethyl-8-hydroxyquinoline hydrochloride

Formaldehyde (8 ml of a 37% solution) was added to a solution of 8-hydroxyquinoline in concentrated hydrochloric acid (7.3 g in 8 ml) and the resulting solution was saturated with hydrochloric acid gas for 2 to 3 hours. A bright yellow crystalline compound separated. Yield 60%. Calcd. for $C_{10}H_9NOCl_2$: C, 52.20; H, 3.95; Found: C, 51.98; H, 3.95; decomposes above 283 °C. 8-Hydroxyquinaldine could also be chloromethylated under the same conditions, and the product obtained was probably 7-chloromethyl-8-hydroxyquinaldine hydrochloride. Yield 58%. Calcd. for $C_{11}H_{11}NOCl_2$: C, 54.11; H, 4.54; Found: C, 53.85; H, 4.62.

Powder diffraction lines

For purposes of identification, X-radiograms of 7-chloromethyl-8-hydroxyquinoline hydrochloride and 7-chloromethyl-8-hydroxyquinaldine hydrochloride, were obtained by the powder diffraction method using a 11.483 cm diameter camera with Straumanis mounting and filtered copper Kα radiation. The patterns were indicative of large unit cells with low symmetry. The interplanar distances of the twelve strongest lines for each compound are listed below.

8-Hydroxyquinoline compound

I/I_0	0.5	0.8	0.8	0.7	0.7	1.0	0.5	0.5	0.5	0.6	0.7	0.6
d	8.63	7.40	4.21	3.86	3.71	3.53	2.707	2.587	2.510	2.438	2.110	1.683

8-Hydroxyquinaldine compound

I/I_0	0.8	0.8	0.7	0.7	1.0	0.7	0.7	0.8	0.6	0.6	0.6	0.6
d	10.15	8.30	5.91	3.82	3.56	3.16	2.94	2.750	2.430	2.340	1.973	1.845

Preparation of 7-hydroxymethyl-8-hydroxyquinoline

An aqueous solution of 7-chloromethyl-8-hydroxyquinoline hydrochloride was neutralized with 1 : 4 ammonia until the solution was distinctly alkaline to litmus. On standing for a few hours, a precipitate was obtained which was filtered and recrystallized from ethyl alcohol. Yield 45%. Calcd. for $C_{10}H_9NO_2$: C, 68.54; H, 5.18; N, 8.00; Found: C, 67.95; H, 5.10; N, 8.05; m.p. 123° C.

Preparation of 5-bromo-7-bromomethyl-8-hydroxyquinoline

Bromine was added dropwise and with rapid stirring to an aqueous solution of 7-chloromethyl-8-hydroxyquinoline hydrochloride, until a precipitate was obtained, which was filtered and recrystallized from ethyl alcohol. Yield 55%. Calcd. for $C_{10}H_7NOBr_2$: C, 37.88; H, 2.23; N, 4.42; Found: C, 37.70; H, 2.19; H, 4.48; m.p. 192° C.

Qualitative and sensitivity tests

An aqueous 1% solution of 7-chloromethyl-8-hydroxyquinoline hydrochloride was used for both the qualitative and sensitivity tests. 1% solutions of the following metal ions were used in these tests:

Co^{+2}, Fe^{+3}, Ni^{+2}, Cd^{+2}, Zn^{+2}, Cu^{+2}, Mn^{+2}, Bi^{+3}, Ag^{+}, Pb^{+2}, Al^{+3}, Ca^{+2}, Ba^{+2}, Mg^{+2}, Cr^{+3}, VO^{+2} and UO_2^{+2}.

DISCUSSION

When formaldehyde reacted with a hydrochloric acid solution of 8-hydroxyquinoline in the presence of hydrochloric acid gas, it was found that the hydrochloride of a chloromethyl derivative of 8-hydroxyquinoline was obtained. This compound is most probably 7-chloromethyl-8-hydroxyquinoline hydrochloride. Attempts to obtain the free base from this hydrochloride resulted in a partial or complete conversion of the chloromethyl group into a hydroxymethyl group. This indicated that the use of the chloromethyl derivative as an analytical reagent for metal ions would be limited to acid or neutral solutions. Bromination of 7-chloromethyl-8-hydroxyquinoline hydrochloride gave a dibromo compound instead of the expected monobromo derivative. This dibromo compound is probably 5-bromo-7-bromomethyl-8-hydroxyquinoline.

Qualitative tests were carried out with an aqueous solution of 7-chloromethyl-8-hydroxyquinoline hydrochloride. At pH 1.0 (dilute hydrochloric acid solution), Fe^{+3} and VO^{+2} ions formed green chelates. None of the other metal ions used gave a positive reaction at this pH. At pH 4.6 (acetic acid-acetate buffer), the following metal ions formed precipitates or colorations: Fe^{+3}, Co^{+2}, Ni^{+2}, Cd^{+2}, Zn^{+2}, Cu^{+2}, Mn^{+2}, Bi^{+3}, VO^{+2}, UO_2^{+2}, Ag^{+} and Pb^{+2}. The following metal ions did not react at pH 4.6: Al^{+3}, Ca^{+2}, Ba^{+2}, Mg^{+2} and Cr^{+3}.

The minimum concentrations of metal ions (in μg/ml), capable of reacting with the 7-chloromethyl-8-hydroxyquinoline hydrochloride, were determined by the method described by IRVING, BUTLER AND RING[8]. These minimum concentrations at pH 1.0 were: Fe^{+3}, 0.25; VO^{+2}, 0.16; and at pH 4.6 were: Co^{+2}, 5.8; Fe^{+3}, 0.8; Ni^{+2}, 5.8; Cd^{+2}, 5.8; Zn^{+2}, 6.6; Cu^{+2}, 4.2; Pb^{+2}, 5.8; VO^{+2}, 0.16; UO_2^{+2}, 2.5.

SUMMARY

The reaction of formaldehyde on a hydrochloric acid solution of 8-hydroxyquinoline, in the presence of hydrochloric acid gas, gave a chloromethyl derivative which is probably 7-chloromethyl-8-hydroxyquinoline hydrochloride. This compound is readily converted into the 7-hydroxymethyl derivative in alkaline solution. The 7-chloromethyl compound has been investigated as an analytical reagent for metal ions in acid solutions.

RÉSUMÉ

La réaction du formaldéhyde sur l'hydroxy-8 quinoléine en solution dans l'acide chlorhydrique, en présence d'acide chlorhydrique gazeux, donne un dérivé chlorométhylé, problablement le chlorhydrate de la chlorométhyl-7-hydroxy-8 quinoléine. Ce composé est rapidement transformé en dérivé 7-hydroxyméthylé, en solution alcaline. Le 7-chlorométhylcomposé a été examiné comme réactif analytique des cations, en solutions acides.

ZUSAMMENFASSUNG

Die Reaktion des Formaldehydes mit 8-Hydroxychinolin in salzsaurer Lösung in Gegenwart von gasförmiger Salzsäure, gibt ein Chloromethylderivat, wahrscheinlich das Hydrochlorid des 7-Chloromethyl-8-hydroxychinolins. Diese Verbindung wird in alkalischer Lösung schnell in das 7-Hydroxymethyl-Derivat übergeführt. Die 7-Chloromethylverbindung wurde in sauren Lösungen als analytisches Reagens für Kationen untersucht.

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OXIDATIONS WITH ALKALINE PERMANGANATE USING MONOVALENT THALLIUM FOR THE BACK-TITRATION

III. ESTIMATION OF TRIVALENT ARSENIC

by

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In estimating arsenite with alkaline permanganate, STAMM[1] and HEREDIA[2], mix the solution with an excess of permanganate in alkaline medium, and titrate back the excess of oxidant with formate. Formate reduces permanganate to the manganate[3,4] state and the accuracy of such a process necessitates that reduction of permanganate by the material to be estimated should not go further than that stage. Whether or not this is the case depends much on the alkali concentration, the reducing power of the material under investigation and the amount of Ba^{+2} present. The means of establishing conditions favouring a quantitative reaction is found by studying the reaction between $KMnO_4$ and arsenite. Difficulties are further overcome by carrying out the reduction of MnO_4^{-2} to Mn^{+4} in presence of telluric acid using monovalent thallium[5] for back-titrating excess permanganate.

EXPERIMENTAL

The experimental technique and the preparation of permanganate solutions is essentially the same as described previously[4].

The arsenite solutions were prepared by dissolving the c.p. product in twice-distilled water. The arsenite content was estimated by bromate, both volumetrically and potentiometrically[6,7].

The reaction between permanganate and arsenite as studied in this paper consists in the reduction of $KMnO_4$ with AsO_3^{-3}:

(a) in absence of Ba^{+2} ions

(b) in presence of telluric acid, and

(c) in presence of Ba^{+2} ions.

The estimation of arsenic is further carried out by mixing the arsenite solution to a sufficient quantity of $KMnO_4$ under the proper conditions, followed by titrating excess oxidant with monovalent thallium.

RESULTS

I. Reduction of $KMnO_4$ in absence of Ba^{+2} ions

Reduction of MnO_4^- ions with arsenite leads to the formation of MnO_2 without any sign of formation of manganate even at the higher alkalinities; this is seen also in the disappearance of the inflection corresponding to manganate. This is apparently due to the strong reducing power of arsenite in alkaline medium. The redox potential of the AsO_4^{-3}/AsO_3^{-3} couple at unit OH^- amounts to —0.67 volt as compared with

0.588 volt for the MnO_4^-/MnO_2 system[8]. From these potential values, the equilibrium constant of the reaction and its degree of completion amounts to $1 \cdot 10^{-128}$ and $2.6 \cdot 10^{-26}$ respectively.

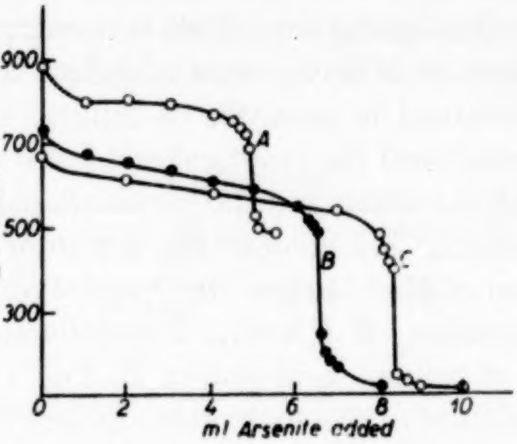

Fig. 1. (A) Titration of 10 ml 0.1266*N* $KMnO_4$ in 1*N* NaOH with 0.051*N* $NaAsO_2$ in presence of Ba^{+2} ions.
(B) Titration of 10 ml 0.0555*N* $KMnO_4$ in 1*N* NaOH with 0.051*N* $NaAsO_2$ in the absence of Ba^{+2} ions and telluric acid.
(C) Titration of 10 ml 0.1422*N* $KMnO_4$ in 2*N* NaOH with 0.102*N* $NaAsO_2$ in presence of telluric acid.

TABLE I

TITRATION OF $KMnO_4$ WITH SOD. META-ARSENITE IN ABSENCE OF TELLURIC ACID AND BARIUM IONS

NaOH	*Max. inflec. per 0.1 ml arsenite mV*	*Theor. end-point ml*	*Exptl. end-point ml*	*Error %*
Titration of 10.0 ml 0.1266*N* $KMnO_4$ with 0.102*N* $NaAsO_2$:				
0.1*N*	164	7.45	7.87	5.64
0.5*N*	201	7.45	7.55	1.39
1*N*	104	7.45	7.52	0.94
2*N*	136	7.45	7.43	−0.27
3*N*	89	7.45	7.42	−0.40
3.5*N*	58	.45	7.20	−3.35
Titration of 5.0 ml 0.02532*N* $KMnO_4$ with 0.0102*N* $NaAsO_2$:				
2*N*	137	7.45	7.35	−1.34
2.5*N*	116	7.45	7.10	−4.70
Titration of 10.0 ml 0.0111*N* $KMnO_4$ with 0.0102*N* $NaAsO_2$:				
0.5*N*	182	6.54	6.63	1.37
0.7*N*	132	6.54	6.56	0.31
1*N*	182	6.5	6.30	−3.67
Titration of 10.0 ml 0.0555*N* $KMnO_4$ with 0.051*N* $NaAsO_2$:				
0.5*N*	216	6.54	6.50	−0.61
1*N*	243	6.54	6.57	0.46
1.5*N*	150	6.54	6.52	−0.30
Titration of 10.0 ml 0.0222*N* $KMnO_4$ with 0.0204*N* $NaAsO_2$:				
0.5*N*	200	6.54	6.62	1.22
1*N*	266	6.54	6.54	nil
1.5*N*	266	6.54	6.45	−1.37

The titration curves (curve C, Fig. 1) obtained under these conditions are smooth and characterized by sharp inflections at the MnO_2 stage, which coincide with the theoretical values in 2–3N NaOH. At lower alkalinities the end-points occur later than the theoretical, probably due to partial formation of Mn_2O_3 and the errors increase in magnitude on decreasing the alkali concentration. At alkalinities higher than 3N autodecomposition of $KMnO_4$ occurs leading to earlier end-points.

The best results are obtained in presence of telluric acid. In this latter case no manganese dioxide separates[8] and the practical end-point coincides with the theoretical one irrespective of both the alkali and the permanganate concentration or the rate of adding the arsenite solution. The complexing action of telluric acid on manganese dioxide prevents reduction of Mn^{+7} below Mn^{+4} and overcomes the catalytic effect of MnO_2 on the decomposition of $KMnO_4$. The inflections at the end-points are sharper than in absence of telluric acid (curve B, Fig. 1). As in absence of telluric acid no inflection was observed at the manganate state even at the highest alkalinity of 3N. In the presence and absence of telluric acid the reaction is rapid both at the beginning of the titration and at the end-point.

TABLE II

TITRATION OF $KMnO_4$ WITH SODIUM META-ARSENITE IN PRESENCE OF TELLURIC ACID AND ABSENCE OF BARIUM IONS

NaOH	*Max. inflec. per 0.1 ml* AsO_2^- *mV*	*Theor. end-point ml*	*Exptl. end-point ml*	*Error %*
Titration of 10.0 ml 0.1422N $KMnO_4$ with 0.102N $NaAsO_2$:				
1.75N	335	8.36	8.32	−0.48
2N	258	8.36	8.33	−0.36
2.91N	233	8.36	8.31	−0.60
Titration of 10.0 ml 0.01422N $KMnO_4$ with 0.0102N $NaAsO_2$:				
1.5N	71	8.36	8.33	−0.36

II. Reduction of $KMnO_4$ *in presence of* Ba^{+2} *ions*

Contrary to previous cases studied[4], and obviously because of the strong reducing power of arsenite, reduction of $KMnO_4$ could not be easily checked at the manganate state by introducing Ba^{+2} ions. The equilibrium constants of the reaction occurring under these conditions and also the degree of completion are however smaller than those of the reactions performed in absence of Ba^{+2} ions. These values as calculated from the E'_0 values of the systems involved, *viz.*
E_0 $(AsO_4^{-3}/AsO_3^{-3}) = -0.67$ V and $E_0(MnO_4^-/MnO_4^{-2}) = 0.56$[8],
amount to $1.7 \cdot 10^{-42}$ and $1.2 \cdot 10^{-14}$ respectively. Addition of an amount of Ba^{+2} equivalent to both arsenate and manganate formed in presence of 1N NaOH did not lead to an inflection at the manganate state. Further, the pink colour of permanganate remained visible even after the manganate inflection has been overstepped. However, by increasing the concentration of Ba^{+2} three or five-fold and decreasing the arsenite concentration

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to 0.0255*N* and the permanganate to 0.05*N*, almost quantitative reduction could be obtained (curve A, Fig. 1). These difficulties render arsenite an unsuitable reagent for back-titrating permanganate in alkaline solution. This confirms the previous observations of HEREDIA[2] who prefers sodium formate to sodium arsenite. Further, although the reaction takes place rapidly at the beginning of the titration, it slows at the end-point, needing from 15-20 min for the attainment of equilibrium.

TABLE III

TITRATION OF $KMnO_4$ WITH $NaAsO_2$ IN PRESENCE OF BARIUM IONS

NaOH	*5% Ba^{+2} ml*	*Max. inflec. per 0.1 ml AsO_2^- mV*	*Theor. end-point ml*	*Exptl. end-point ml*	*Error %*
Titration of 10.0 ml 0.1422*N* $KMnO_4$ with 0.102*N* $NaAsO_2$:					
0.5*N*	excess	142	2.79	3.38	21.15
1.5*N*	8	142	2.79	3.32	19.00
1.5*N*	7	134	2.79	3.12	11.7
Titration of 10.0 ml 0.1422*N* $KMnO_4$ with 0.0714*N* $NaAsO_2$:					
1*N*	15	136	3.98	4.15	4.27
1.5*N*	10	99	3.98	4.96	16.33
Titration of 10.0 ml 0.1261*N* $KMnO_4$ with 0.051*N* $NaAsO_2$:					
1*N*	9	82	4.94	4.97	0.60
1.5*N*	10	150	4.94	4.96	−0.40
Titration of 5.0 ml 0.1261*N* $KMnO_4$ with 0.0255*N* $NaAsO_2$:					
0.7*N*	10	165	4.94	4.90	−0.81
Titration of 10.0 ml 0.0504*N* $KMnO_4$ with 0.0255*N* $NaAsO_2$:					
0.7*N*	10	180	3.95	3.94	−0.25
Titration of 10.0 ml 0.0504*N* $KMnO_4$ with 0.0102*N* $NaAsO_2$:					
0.7*N*	10	143	9.88	9.83	−0.51

III. Estimation of arsenite by oxidation with permanganate using monovalent thallium for titrating excess oxidant

As was previously shown, monovalent thallium can be used for back-titrating $KMnO_4$ in either the presence or absence of Ba^{+2} ions and in the presence of telluric acid[5]. We developed a method for the estimation of arsenic based upon these facts. Arsenite solutions are mixed with $KMnO_4$, either in the presence of Ba^{+2} ions three times that equivalent to the arsenite and permanganate present and 1*N* NaOH, or in absence of Ba^{+2} ions and 1*N* to 2*N* NaOH. In both cases the arsenite is added dropwise and the excess $KMnO_4$ titrated with Tl^+. In presence of Ba^{+2} ions $KMnO_4$ is reduced to manganate whereas in their absence it is reduced to Mn^{+4}. Better results, as can be seen from the data in Table IV, are obtained in this latter case. Small quantities of arsenic as low as 1 mg could be estimated with an accuracy of 0.5%.

TABLE IV

DETERMINATION OF As^{+3} USING Tl^{+} FOR BACK-TITRATING $KMnO_4$

Vol. & Normality of As^{+3} soln.	*As added mg*	*As found mg*	*Error %*
$KMnO_4$ = 5.0 ml 0.1111*N*, Tl^{+} = 0.0307*N*, telluric acid present			
10 ml × 0.0102*N*	3.820	3.805	−0.40
15 ,, ,,	5.730	5.720	−0.17
1 ,, ,,	0.382	0.381	−0.20
3 ,, ,,	1.146	1.140	−0.54
$KMnO_4$ = 5 ml 0.1132*N*, Tl^{+} = 0.0334*N*			
5 ml × 0.0204*N*	3.820	3.820	nil
10 ,, ,,	3.640	7.640	nil
0.5 ,, × 0.102*N*	1.910	1.905	−0.24
1 ,, × 0.152*N*	3.820	3.820	nil
2 ,, × 0.102*N*	7.640	7.600	−0.50
Determination of As^{+3} using Tl^{+} for back-titration in presence of Ba^{+2} :			
1 ml × 0.0102*N*	0.382	0.381	−0.20
5 ,, ,,	1.910	1.900	−0.50
2 ,, × 0.0204*N*	1.528	1.528	nil
3 ,, ,,	2.292	2.291	−0.55

SUMMARY

In absence of Ba^{+2} ions arsenite reduces $KMnO_4$ in alkaline medium to MnO_2 without the appearance of an inflection at the manganate state. Reduction could be checked at the manganate in presence of 1*N* NaOH and Ba^{+2} equal to 3 times that equivalent to MnO_4^{-2} and arsenate, and when dilute arsenite solutions are applied *viz.*0.02*N*. In absence of Ba^{+2} ions the end-points are attained later than the MnO_2 stage except in 2-3*N* NaOH. In presence of telluric acid good results are obtained at all alkalinities whence reduction is checked at Mn^{+4}.

As^{+3} could be estimated also by mixing with $KMnO_4$ either in the presence of Ba^{+2} ions + 1*N* NaOH or in absence of Ba^{+2} ions + 1.5-3*N* NaOH and back-titrating the excess oxidant with monovalent thallium.

RÉSUMÉ

En l'absence d'ions Ba^{+2}, l'arsenite en solution alcaline réduit $KMnO_4$ en MnO_2 sans qu'apparaisse le stade manganate. La réduction, en solution 0.02*N*, peut s'arrêter au manganate en présence de NaOH *N* et Ba^{+2}, en concentration égale à 3 fois celle de MnO_4^{-2}. En l'absence de Ba^{+2}, les points finals sont obtenus après le stade MnO_2 sauf dans NaOH 2-3*N*. En présence d'acide tellurique, la réduction en Mn^{+4} s'effectue à toutes les alcalinités. As^{+3} peut être dosé par $KMnO_4$, soit en présence de Ba^{+2} + NaOH *N*, soit sans Ba^{+2}, dans NaOH 1.5-3*N*; l'excès d'oxydant est ensuite titré avec Tl^{+}.

ZUSAMMENFASSUNG

Bei Abwesenheit von Ba^{+2} Ionen, reduziert Arsenit in alkalischer Lösung $KMnO_4$ zu MnO_2, ohne dass das Manganat-Stadium in Erscheinung tritt. In 0.02*N* Lösung, kann die Reduktion in Gegenwart von *N* NaOH und Ba^{+2} in einer Konzentration die das Dreifache derjenigen des MnO_4^{-2} beträgt beim Manganat anhalten. Bei Abwesenheit von Ba^{+2} werden die Endpunkte nach

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dem MnO_2 Stadium erhalten, ausser in 2-3N NaOH. In Gegenwart von Tellursäure, ist die Reduktion zu Mn^{+4} bei allen Alkalinitäten durchführbar. As^{+3} kann mit $KMnO_4$ bestimmt werden, sei es in Gegenwart von Ba^{+2} + N NaOH, sei es ohne Ba^{+2}, in 1.5-3N NaOH; der Überschuss des Oxydationsmittels wird darauf mit Tl^+ titriert.

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5 : 6-BENZOQUINALDINIC ACID AS AN ANALYTICAL REAGENT

I. DETERMINATION OF THORIUM AND ZIRCONIUM

by

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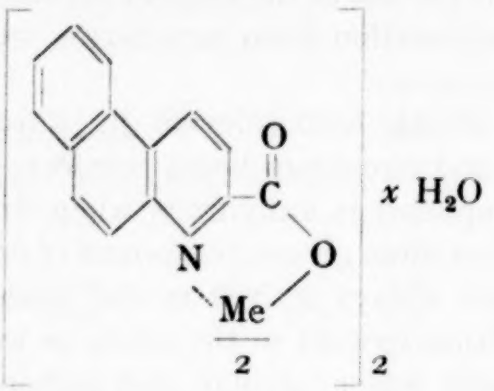
The reagent, 5 : 6-benzoquinaldinic acid, m.p. 187° C, is highly soluble in alcohol and in acetic acid, less soluble in hot water and sparingly so in cold water. Under controlled pH conditions, it can be used to precipitate completely almost all the metals. Of them, copper gives a green precipitate; zinc, magnesium, calcium, strontium, barium, silver, mercury, lead and cadmium, white precipitates; cobalt, cream coloured; nickel, greenish and manganese, yellow.

The copper complex which is sparingly soluble in dilute mineral acids or acetic acid, is soluble in a large excess of ammonia and in solutions of alkali cyanide. All other complexes are more or less soluble in dilute acids. Such solubility in dilute acids is also shown by the complexes of iron(III), aluminium, antimony(III), bismuth, uranium (UO_2^{+2}), zirconium, thorium, beryllium, rare earths and tin(II), which are not precipitated from ammoniacal tartrate solutions. The chromic complex though soluble in ammoniacal tartrate medium is sparingly soluble even in fairly strong acids. Zinc, manganese, nickel, cobalt, silver, mercury and cadmium complexes are soluble in solutions of alkali cyanide and those due to lead and mercury also dissolve in an excess of ammonium acetate. The zinc complex is soluble also in an excess of ammonia, as is cadmium, and in alkali. Cobalt, nickel and manganese, on the other hand, are insoluble in ammonia. In moderately strong caustic soda solution both the nickel and manganese complexes are decomposed to their hydroxides, but that of cobalt, dissolves on heating and reappears on cooling. The lithium and thallous complexes are soluble in dilute acids and in hot water as are the complexes of beryllium, barium, calcium and strontium. Vanadate, molybdate and tungstate are not precipitated by the reagent from an alkaline solution, but in the presence of acid they give yellowish white precipitates which are sparingly soluble in excess of dilute acids. All the metal complexes, except that of beryllium, have been found to be insoluble in organic solvents such as ethyl and amyl alcohols, ether, chloroform, ethyl acetate, benzene, carbon disulphide and carbon tetrachloride. The beryllium complex on the other hand is fairly soluble in ethyl acetate and acetone and slightly so in ethyl alcohol and chloroform.

The pH regions for complete precipitation of copper, cadmium, zinc, manganese, nickel and cobalt are respectively at and over 0.82, 3.12, 2.85, 2.90, 3.00 and 3.24. Even at a pH value of about 10 they may be accurately determined. Copper is completely precipitated even from cupro-ammonium salt solutions in the presence of an excess of ammonium salt. The complexes when dried at about 110° C are hydrated and may be represented by (I).



Where Me is a bivalent metal cation

(I)

They dehydrate at higher temperatures, *e.g.*, the copper complex becomes anhydrous at 168° C, cadmium at 130° C, zinc at 186° C, cobalt at 150° C, while at 180° C nickel and manganese lose 7.23% and 6.60% of water respectively. The degree of hydration is independent of the pH except in the case of cadmium where the highly crystalline hydrated complex precipitated at a pH lower than 3.85, contains 1.5 moles of water, but when precipitated at a higher pH it retains water to the extent of about 2 moles, which is eliminated only at temperatures above 165° C. This retention of extra water is due perhaps to the nature of the precipitate.

Recently it has been observed that the mercury complex, like that of silver, is anhydrous at 100° C and stable up to 150° C; it is completely precipitated over the pH range 1.9 to 6.0. By the proper control of pH and by the help of a complexing agent it is easily separated from quite a large number of elements[2].

Of the three reagents, *α*-picolinic acid[3], quinaldinic acid[4] and 5:6-benzoquinaldinic acid[5] having the same functional groups $=N-$ and $-\overset{\overset{O}{\|}}{C}-OH$, ortho to each other, the salts of quinaldinic acid are less soluble than those of *α*-picolinic acid but far more soluble than those of 5:6-benzoquinaldinic acid owing to the weighting effect. As expected, the ferrous salt of *α*-picolinic acid in solution is highly soluble and stable but the ferrous salts of the other two acids are less stable and far less soluble. Here the stability of the ferrous salt in solution decreases with the increase in the molecular weight of the reagent. Thus the ferrous picolinate complex could not be isolated from water or alcoholic solution in which it is highly soluble, whereas the ferrous salts of the other two reagents easily separate from aqueous solutions and the ferrous picolinate is stable even at a pH of 6.7; the other ferrous salts are easily decomposed at that pH. Here it must be stated that neither great stability nor pronounced solubility in organic solvents is necessarily a characteristic feature of inner complex salts as is often erroneously assumed[1]. Alkali cyanide, because it forms complexes of the type $[Fe(org)_2(CN)_2]K_2$ (where H org is the acid organic reagent) with the ferrous salts of these reagents[3,4,5], dissolves the ferrous complexes and besides intensification of the colour, stabilizes the colour system so formed. With 5:6-benzoquinaldinic acid, the region of maximum absorption is at 515 mμ and the colour intensity varies with the concentration of ferrous ion.

In previous communications, it was shown that 5:6-benzoquinaldinic acid could be used for the separation and determination of copper and cadmium[6,7]. Also the reagent was found to be effective for the estimation of zinc, cobalt, nickel and manganese[8] and for the separation of copper and cadmium from various elements[9,10]. The subject matter of the present investigation is the use of the reagent for the determination of thorium and zirconium and their separation from rare earths, alkaline earths and magnesium.

Thorium and zirconium are precipitated in weakly acid solution by 5:6-benzoquinaldinic acid; the precipitation of thorium and zirconium being complete above pH 3.0 and 1.8 respectively. The thorium compound is anhydrous when dried at 110° C and of composition $Th(C_{14}H_8O_2N)_4$, but zirconium gives a compound of variable composition and so zirconium precipitates were always ignited to the oxide. The thorium precipitate, on the other hand, was either ignited to the oxide or weighed as $Th(C_{14}H_8O_2N)_4$ after successive washings with water, alcohol and acetone.

Separation of thorium and zirconium from the rare earths can be carried out by simple precipitation from acid solution, and separation from magnesium and alkaline earths can be achieved from solutions containing ammonium salts.

EXPERIMENTAL

Reagents and apparatus

5:6-benzoquinaldinic acid was prepared according to the modified method of MAJUMDAR AND MALLICK[6] and purified by recrystallization from glacial acetic acid. A 1% alcoholic solution of the reagent of m.p. 187° C was used as precipitant.

Solutions of the rare earths were prepared from a thoriumfree rare earth mixture prepared from monazite. All other chemicals used were of reagent grade and the strengths of the solutions of thorium, zirconium, rare earth mixture, strontium, barium and magnesium were determined by standard gravimetric procedures. Calcium was determined volumetrically. pH measurements were made with a bench model pH meter.

Composition of the thorium and zirconium salt of the reagent

An alcoholic solution of the reagent was added dropwise to acid solutions of thorium and zirconium until the precipitation was complete. The precipitates were then washed several times with hot water and then with hot alcohol to free them from excess reagent. The precipitates were dried at 110° C until their weights were constant. Weighed amounts of precipitates were ignited to the oxide. Thus the thorium compound was found to have the composition $Th(C_{14}H_8O_2N)_4$ (% ThO_2 calc., 23.54; found, 23.50, 23.52) and stable even at 150° C. The zirconium complex was found to vary in composition from sample to sample.

Procedure

Acid solutions of thorium or zirconium after dilution to about 200 ml were adjusted to the desired pH and heated to boiling. To this hot solution was added, with stirring dropwise, the reagent solution until precipitation was complete. The solution was then kept on a hot-plate for about fifteen minutes, filtered, washed with hot 1% ammonium nitrate solution, dried, ignited and weighed (see Tables I and II).

For direct weighing of thorium as $Th(C_{14}H_8O_2N)_4$, the thorium complex, after precipitation and digestion, was filtered through a weighed gooch crucible, washed with hot water, then with hot alcohol and finally thrice with acetone. It was then dried at 110° C and weighed (see Table III). The method of direct weighing has the disadvantage that a thorough washing with hot water and hot alcohol blocks the pores of the crucible pad.

Separation of thorium from rare earths

Phosphate-free acid solution containing thorium and the rare earths with cerium in the trivalent state, rendered so by hydrogen peroxide, was diluted to about 250 ml, the pH adjusted to the yellow colour of methyl orange and heated to boiling. The thorium was precipitated with stirring by the dropwise addition of the reagent. After complete precipitation and digestion for about ten minutes followed the usual procedure referred to above (see Table IV).

Separation of zirconium from rare earths was carried out in the same way as for thorium, cresol red being used as indicator instead of methyl orange (see Table V).

Separation from alkaline earths and magnesium was effected according to procedures for the separation from the rare earths with the previous addition of about 5 g of ammonium chloride to the solution (see Table VI).

TABLE I

DETERMINATION OF THORIUM

ThO_2 present mg	pH	ThO_2 found mg	Error mg
71.4	4.3	71.3	−0.1
71.4	4.0	71.5	+0.1
71.4	3.8	71.4	0.0
71.4	3.4	71.2	−0.2
71.4	3.0	71.3	−0.1
71.4	2.5	70.2	−1.2

TABLE II

DETERMINATION OF ZIRCONIUM

ZrO_2 present mg	pH	ZrO_2 found mg	Error mg
26.5	3.0	26.6	+0.1
26.5	2.8	26.5	0.0
26.5	1.8	26.7	+0.2

pH values less than 1.8 give a non-crystalline precipitate.

TABLE III

ThO_2 present mg	Th-compound mg	ThO_2 found mg
27.6	119.0	27.9
27.6	118.6	27.8
27.6	118.6	27.8

TABLE IV

SEPARATION OF THORIUM FROM RARE EARTHS

ThO_2 present mg	R_2O_3 present mg	ThO_2 found mg	Error mg
71.4	101.2	71.5	+0.1
71.4	202.4	71.3	−0.1
35.7	50.6	35.6	−0.1
27.6	375	27.5	−0.1
27.6	375	27.7	+0.1

TABLE V

SEPARATION OF ZIRCONIUM FROM RARE EARTHS

ZrO_2 present mg	R_2O_3 present mg	ZrO_2 found mg	Error mg
26.5	37.5	26.5	0.0
26.5	37.5	26.6	+0.1
26.5	375	26.6	+0.1
26.5	375	26.4	−0.1

TABLE VI

SEPARATION OF THORIUM AND ZIRCONIUM FROM MAGNESIUM AND ALKALINE EARTHS

ThO_2 present mg	*Ion added mg*	*ThO_2 found mg*	*Error mg*
27.6	Ca-100 R_2O_3-187.5	27.9	+0.3
27.6	Mg-100 R_2O_3-187.5	27.7	+0.1
27.6	Ca-100	27.5	−0.1
27.6	Ba-100	27.6	0.0
27.6	Sr-100	27.7	+0.1
ZrO_2 present mg		*ZrO_2 found mg*	
26.5	Ca-100	26.4	−0.1
26.5	Mg-100	26.7	+0.2
26.5	Ba-100	26.6	+0.1
26.5	Sr-100	26.5	0.0

Further work of this nature is in progress.

SUMMARY

Thorium and zirconium are determined in the presence of rare earths, alkaline earths and magnesium, when precipitated from weakly acid solution with 5:6-benzoquinaldinic acid. Thorium is completely precipitated at pH 3.0 as $Th(C_{14}H_8O_2N)_4$, but though zirconium is precipitated at the lower pH of 1.8, its composition is not stoichiometric and hence is ignited to the oxide before weighing. Co-precipitation of magnesium and alkaline earths is prevented by the addition of ammonium chloride.

RÉSUMÉ

Le thorium et le zirconium peuvent être dosés, en présence des éléments des terres rares, alcalino-terreux et du magnésium, par précipitation en solution faiblement acide, au moyen de l'acide 5.6-benzoquinaldinique. Le thorium précipite quantitativement au pH 3.0, sous forme de $Th(C_{14}H_8O_2N)_4$, tandis que le zirconium précipite au pH 1.8, pour donner un corps de composition mal définie. Il faut le calciner en oxyde avant d'effectuer la pesée. La coprécipitation du magnésium et des éléments alcalino-terreux est empêchée par addition de chlorure d'ammonium.

ZUSAMMENFASSUNG

Das Thorium und das Zirkonium können in Gegenwart von seltenen Erden, Erdalkalien und Magnesium bestimmt werden, mittels einer Fällung in schwachsaurer Lösung mit Hilfe von 5.6-Benzochinaldinsäure. Das Thorium fällt quantitativ bei pH 3.0 in Form von $Th(C_{14}H_8O_2N)_4$ aus, während das Zirkonium bei pH 1.8 in Form einer Verbindung ausfällt, deren Zusammensetzung nicht stöchiometrisch ist. Vor dem Wägen muss man diese zu Oxyd kalzinieren. Die Kopräzipitation von Magnesium und den Erdalkalien wird durch eine Zugabe von Ammoniumchlorid verhindert.

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MÉTHODE DE DOSAGE DU NICKEL MÉTALLIQUE EN PRÉSENCE DE COMPOSÉS OXYDÉS DE NICKEL DANS DES MATIÈRES COMPLEXES (MINERAIS)

par

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I. INTRODUCTION — OBJET DU PRÉSENT TRAVAIL

L'étude des possibilités de traitement métallurgique d'un minerai oxydé pauvre de nickel ayant fait apparaître qu'un procédé en deux stades (réduction du nickel à l'état métallique, puis formation de nickel-carbonyle à décomposer ultérieurement) pouvait être envisagé, il était indispensable que les deux stades opératoires fussent contrôlés séparément.

Le contrôle des résultats expérimentaux obtenus au premier stade (réduction des composés oxydés de nickel en nickel métallique) exigeait les déterminations quantitatives du nickel oxydé et du nickel métallique dans un même échantillon.

Il était impossible d'atteindre ce but en dosant le nickel total, puis l'oxygène contenu dans les oxydes de Ni, de nombreux composés oxydés autres que ceux de Ni étant présents dans la matière étudiée en proportions variables suivant le degré de réduction.

Des recherches bibliographiques poussées ne nous ont fourni aucune indication précise et nous avons dû, dans ces conditions, essayer de mettre au point une méthode d'analyse permettant de doser séparément, dans un minerai complexe, le nickel métallique d'une part, et le nickel dans l'ensemble de ses combinaisons oxydées (oxydes, silicates) d'autre part.

Le problème a été résolu en déterminant dans quelles conditions il est possible de mettre en solution la totalité du nickel métallique en laissant inaltérés tous les composés oxydés de Ni. On dose alors le nickel total et le nickel mis sélectivement en solution dans ces conditions, et par différence, on obtient le nickel présent sous forme oxydée.

Divers essais de mise en solution sélective du nickel métallique dans différents milieux ont échoué. Ils ont néanmoins été utiles en faisant apparaître des différences marquées dans les vitesses de mise en solution du nickel métallique d'une part (dissolution rapide) et des composés oxydés de nickel d'autre part (dissolution très lente). Malheureusement, la vitesse de dissolution du nickel métallique diminue très rapidement au fur et à mesure de l'abaissement de sa teneur dans les solides résiduels, et la dissolution complète du nickel métallique n'a jamais pu être atteinte sans qu'une fraction plus ou moins importante, mais jamais négligeable, du nickel oxydé entrât aussi en solution.

Les divers milieux dissolvants essayés ont montré l'influence primordiale de la durée de l'opération, qui doit être assez importante pour que tout le nickel métallique soit mis en solution. Il était donc obligatoire de ne retenir que ceux qui, après des actions de longue durée, ne permettaient rigoureusement aucune mise en solution du nickel oxydé.

Il apparut assez rapidement qu'un milieu remplissant assez bien ces conditions était une solution de chlorure mercurique. Des recherches systématiques ont permis de préciser la nature exacte de la solution à utiliser et les conditions de son emploi.

Au cours de ces recherches, diverses modifications ont été apportées à la solution de chlorure mercurique. Le but poursuivi était surtout l'obtention d'une méthode donnant plus rapidement des résultats suffisamment exacts. En particulier, le pH de la solution a été augmenté par addition d'un complexant du mercure, pour éviter sa précipitation. Le complexant choisi a été le cyanure de potassium.

Les essais de mise en solution sélective du nickel métallique par la solution ainsi modifiée n'ont donné aucun résultat positif. Toutefois, en abaissant par addition d'acide chlorhydrique le pH d'une solution contenant du chlorure de mercure(II) et du cyanure de potassium, on a constaté qu'il était possible de dissoudre sélectivement le nickel métallique dans certaines conditions. Celles-ci ont été précisées et ont conduit à l'obtention d'une seconde méthode permettant de doser le nickel métallique en présence de ses combinaisons oxydées.

Dans le présent travail sont décrits succinctement:

1) Les résultats des essais ayant conduit à l'obtention de deux moyens de mise en solution sélective du nickel métallique;
2) Les méthodes d'analyse qui en ont été déduites;
3) La vérification de ces méthodes appliquées à des mélanges synthétiques d'abord, à des minerais complexes contenant une quantité connue de nickel métallique, ensuite.

II. DÉTERMINATION DES POSSIBILITÉS DE MISE EN SOLUTION SÉLECTIVE DU NICKEL MÉTALLIQUE

A. Produits utilisés

Le nickel métallique est de la poudre de nickel exempte de cobalt et obtenue par réduction par l'hydrogène. Cette poudre ayant pu s'oxyder légèrement pendant le stockage, elle a été chauffée pendant 1 heure 30 à 175-225° C dans un courant d'hydrogène[1].

L'oxyde de nickel est en réalité un mélange d'oxydes NiO et Ni_2O_3 en proportions non définies, l'essentiel étant l'absence absolue de nickel métallique. Le produit, qui sera appelé oxyde de nickel dans cette note, a été obtenu par calcination de $Ni(NO_3)_2 \cdot 6H_2O$, de qualité *p.a.*, pendant 3 heures à 900° C, par porphyrisation en mortier d'agate, et par une nouvelle calcination de 2 heures à 900° C[2]. Le produit final est conservé en exsiccateur.

Les autres réactifs, $HgCl_2$, KCN et HCl, sont tous des produits de qualité *p.a.*

B. Essais de dissolution du nickel métallique

1. Mode opératoire

Peser exactement 0.1000 à 0.1010 g de nickel en poudre. Porter à l'ébullition dans un vase conique surmonté d'un réfrigérant la solution étudiée. Dès que l'ébullition est franche, verser dans la solution la poudre de nickel et maintenir l'ébullition pendant une durée déterminée.

Laisser refroidir et filtrer. Dans le filtrat acidifié par HCl, précipiter le mercure par H_2S, filtrer, chasser H_2S du filtrat par ébullition prolongée et doser Ni par électrolyse en milieu ammoniacal[3].

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2. *Influence de la durée et de la concentration en $HgCl_2$ de la solution*

La première série d'essais a été effectuée avec des solutions dont la concentration en $HgCl_2$ était variable; leur pH variait naturellement en fonction de cette concentration. L'ébullition pendant des durées différentes a donné les résultats suivants:

Solution utilisée	pH	*Durée*	*% Ni dissous*
50 ml $HgCl_2$ à 37 g/l	3.4	15 min	88.0
50 ml $HgCl_2$ à 37 g/l	3.4	2h	97.1
50 ml $HgCl_2$ à 37 g/l	3.4	6h	98.2
50 ml $HgCl_2$ à 25 g/l	3.6	2h	97.6
50 ml $HgCl_2$ à 25 g/l	3.6	6h	100.0
50 ml $HgCl_2$ à 18.5 g/l	3.7	2h	95.0
50 ml $HgCl_2$ à 18.5 g/l	3.7	6h	99.0

Ces résultats montrent que la concentration en $HgCl_2$ de la solution n'a qu'une influence faible, si on la compare à celle de la durée de l'opération. De plus, on voit nettement que la vitesse de dissolution ralentit fortement lorsque la quantité de nickel métallique non encore attaqué est faible.

3. *Influence de la durée de l'expérience et de la quantité de solution*

Pour étudier le facteur „quantité de solution", il a été décidé d'utiliser la solution à 18.5 g/l $HgCl_2$. L'influence de la durée de l'expérience a été observée également. Les résultats ont été les suivants:

Solution utilisée	pH	*Durée*	*% Ni dissous*
75 ml $HgCl_2$ à 18.5 g/l	3.7	15 min	83.4
75 ml $HgCl_2$ à 18.5 g/l	3.7	2h	96.1
75 ml $HgCl_2$ à 18.5 g/l	3.7	6h	100.0
100 ml $HgCl_2$ à 18.5 g/l	3.7	15 min	93.0
100 ml $HgCl_2$ à 18.5 g/l	3.7	2h	100.0

En comparant ces résultats à ceux qui ont été obtenus avec 50 ml de solution (voir 2, ci-dessus), on peut observer que la dissolution totale de la quantité choisie arbitrairement (0.1000 g) de Ni métallique est d'autant plus rapide que le volume de solution employé est grand.

Les deux séries d'essais dont les résultats sont donnés ci-dessus permettent déjà d'affirmer que dans trois cas précis, il est possible de dissoudre 100 % du nickel métallique, lorsqu'on opère dans des conditions bien définies, soit une prise d'essai de 0.1 g de nickel en poudre et une attaque de 6 heures par 50 ml de solution à 25 g/l $HgCl_2$ ou 75 ml de solution à 18.5 g/l $HgCl_2$ ou attaque de 2 heures par 100 ml de solution à 18.5 g/l $HgCl_2$.

La durée de l'attaque étant assez longue, nous avons essayé de réduire cette durée par divers moyens. La seule méthode suffisamment bien étudiée fut l'addition de cyanure de potassium à la solution de chlorure mercurique. De cette façon, il était possible de faire varier le pH de la solution en évitant toute précipitation du mercure. De plus, le cyanure pouvait éventuellement agir comme complexant, et du mercure, et du nickel.

4. *Influence d'une addition de KCN à la solution mercurique*

La solution de base utilisée dans cette série d'expériences était constituée par 100 ml de solution à 18.5 g/l $HgCl_2$, auxquels on ajoutait la quantité de solution à 80 g/l KCN nécessaire pour atteindre le pH voulu.

Les résultats sont résumés ci-dessous:

pH *de la solution utilisée*	*Durée de l'expérience*	% *Ni dissous*
5.2	6h	99.2
6.0	6h	98.2
7.0	6h	33.2
9.0	6h	1.015
10.5	6h	0.625

Ces essais ont montré nettement qu'une élévation de pH réduisait dans des proportions très marquées le pourcentage de Ni dissous après 6 heures. Il est évident que cette voie ne pouvait être suivie pour obtenir le résultat cherché.

Cependant, on peut obtenir un pH plus élevé que le pH naturel de la solution de base en ajoutant du KCN jusqu'à pH 10.5 puis en abaissant le pH par addition de HCl. Cette méthode a fait l'objet de la série d'essais suivante.

5. *Influence du pH d'une solution contenant à la fois $HgCl_2$, KCN et HCl*

La solution de base utilisée dans cette série d'essais était constituée par 100 ml de solution à 18.5 g/l $HgCl_2$ et 25 ml de solution à 80 g/l KCN. Le pH de cette solution est 10.7. Par addition de solution de HCl 6*N*, on obtient la solution de pH voulu.

Les résultats obtenus ont été les suivants:

pH *de la solution utilisée*	*Durée de l'essai*	% *Ni dissous*
4.0	6h	9.26
6.0	15 min	35.6
6.0	6h	47.6
7.0	2h	70.2
7.0	6h	89.7
9.0	2h	84.2
9.0	6h	100.0

Comme on peut le remarquer, l'influence du pH, dans les solutions étudiées, est prépondérant pour la détermination de la vitesse de dissolution. Les chiffres sont à comparer aux résultats des essais effectués en solution $HgCl_2$-KCN. Il semble donc que l'addition de KCN ou de KCN + HCl a une influence très défavorable sur la dissolution de Ni aux pH faibles, tandis qu'aux pH élevés, on peut obtenir une dissolution presque complète dans tous les cas avec un maximum de 100 % pour la solution $HgCl_2$-KCN-HCl de pH 9.

Mais on doit également remarquer que le but que l'on cherchait à atteindre, c'est-à-dire réduire la durée de l'attaque, n'a pu être approché.

C. *Étude de la dissolution de l'oxyde de nickel*

Les résultats acquis jusqu'à présent ont montré que dans des conditions bien définies, il est possible de dissoudre la totalité du nickel métallique. Ces perspectives encourageantes nous ont incité à poursuivre les essais de mise au point de la méthode d'analyse cherchée.

Il était donc nécessaire de voir comment se comporterait l'oxyde de nickel dans les conditions qui ont permis de mettre en solution la totalité du nickel métallique.

1. *Mode opératoire*

Peser exactement 0.1272 à 0.1286 g d'oxyde de Ni (ce qui correspond à 0.100—0.1010 g Ni, le facteur théorique étant 0.786).

Opérer ensuite exactement comme dans le cas du nickel métallique.

2. *Résultats des expériences*

Les expériences de dissolution de l'oxyde de nickel ont été effectuées uniquement avec les solutions et dans les conditions qui ont permis de dissoudre la totalité du nickel métallique. Les résultats ont montré que l'oxyde de nickel ne passait absolument pas en solution lorsque la solution était constituée soit par 100 ml de $HgCl_2$ à 18.5 g/l, avec ébullition de 2 heures, soit par 100 ml de $HgCl_2$ à 18.5 g/l, 25 ml de KCN à 80 g/l et la quantité de HCl 6*N* nécessaire pour obtenir un pH égal à 9.0, avec ébullition de 6 heures.

Dans les autres cas, il passe en solution une quantité non négligeable d'oxyde de nickel.

III. MÉTHODES DE DOSAGE PROPOSÉES

Les résultats des essais exposés ci-dessus permettent de proposer les deux méthodes de dosage suivantes pour déterminer la teneur en Ni métallique de matières contenant des composés oxydés de ce métal:

1. Dans un vase conique de 300 ml, verser 100 ml de solution à 18.5 g/l $HgCl_2$. Porter à l'ébullition sous condenseur. Dès que la solution bout, y verser une prise d'essai du minerai exactement pesée et contenant au maximum 0.1 g de Ni métallique.

Maintenir à l'ébullition pendant 2 heures, puis laisser refroidir. Filtrer. Dans le filtrat, doser le nickel par électrolyse après séparation du mercure et des autres éléments éventuellement dissous[4].

2. Observer le même mode opératoire, mais en utilisant une solution composée de 100 ml de $HgCl_2$ à 18.5 g/l, 25 ml de KCN à 80 g/l et amenée à pH 9 par addition de HCl 6*N*. Dans ce cas, il faudra maintenir l'ébullition pendant 6 heures.

IV. VÉRIFICATION DES DEUX MÉTHODES DE DOSAGE PROPOSÉES

A. *Vérification sur des mélanges synthétiques nickel métallique-oxyde de nickel*

1. *Mode opératoire*

La vérification des deux méthodes proposées ci-dessus a d'abord porté sur des mélanges synthétiques de nickel métallique et d'oxyde de nickel. La prise d'essai était un mélange de ces deux constituants en proportions variables, tel que la quantité totale de nickel contenu soit comprise entre 0.1000 et 0.1010 g.

2. *Essais en solution de $HgCl_2$ à pH 3.7 - 2 heures*

Prise d'essai	*g Ni contenu*	*% Ni métal*	*% Ni métal dosé*
0.0251 g Ni + 0.0954 g NiO	0.10018	20.85	20.32
0.0501 g Ni + 0.0639 g NiO	0.100325	43.9	42.4
0.0752 g Ni + 0.0321 g NiO	0.10043	70.0	68.3

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3. *Essais en solution de $HgCl_2$, KCN et HCl à pH 9 - 6 heures*

Prise d'essai	*Ni contenu* g	*% Ni métallique* *contenu*	*dosé*
0.0252 g Ni + 0.0957 g NiO	0.10042	20.85	21.08
0.0504 g Ni + 0.06365 g NiO	0.10043	44.2	44.25
0.0757 g Ni + 0.0320 g NiO	0.100852	70.25	67.6

4. *Conclusions des essais*

Les résultats ci-dessus montrent que le dosage de Ni métallique en présence d'oxydes de nickel est possible à environ 3 % près par les méthodes proposées. La précision semble être d'autant meilleure que la teneur en Ni métallique est faible, surtout pour la solution $HgCl_2$-KCN-HCl à pH 9.

B. *Vérification sur des mélanges minerai de nickel-nickel métallique*

1. *Conditions opératoires*

Pour cette série d'essais, on a utilisé un minerai oxydé de nickel de composition suivante: Ni 1.72 %; Co 0.10 %; Fe 35.55 %; SiO_2 16.4 %; CaO 2.10 %; MgO 1.08 %; Al_2O_3 13.50 %; Cr 2.28 %; Mn 0.98 %.

Dans ce minerai, le nickel se trouve sous forme d'oxydes et de silicates, mais pas d'aluminate, comme l'a montré une analyse aux rayons X.

Au moyen des deux méthodes d'analyse proposées, il a été vérifié que la teneur en Ni métallique était nulle.

Les essais ont été effectués en mélangeant à ce minerai des quantités variables de nickel métallique en poudre; dans un des essais, on a également ajouté du fer métallique en poudre pour voir quelle pouvait être son influence sur la dissolution du nickel métallique.

2. *Essais en solution de $HgCl_2$ à pH 3.7 - 2 heures*

Prise d'essai	*Ni contenu* g	*% Ni métallique* *contenu*	*dosé*
1.0028 g minerai + 0.0066 g Ni	0.02385	0.654	0.652
1.0044 g minerai + 0.0227 g Ni	0.03998	2.210	2.079
1.0021 g minerai + 0.0139 g Ni + 0.0136 g Fe	0.03114	1.350	1.311

3. *Essais en solution de $HgCl_2$, KCN et HCl à pH 9 - 6 heures*

Prise d'essai	*Ni contenu* g	*% Ni métallique* *contenu*	*dosé*
1.0023 g minerai + 0.0074 g Ni	0.02464	0.733	0.743
1.0037 g minerai + 0.0219 g Ni	0.03916	2.135	2.092
1.0012 g minerai + 0.0140 g Ni + 0.0125 g Fe	0.03122	1.362	1.342

V. CONCLUSIONS

Comme le montrent les résultats expérimentaux exposés ci-dessus, les méthodes proposées pour le dosage du nickel métallique en présence de composés oxydés du nickel dans des matières complexes (minerais) permettent d'obtenir la teneur en nickel métallique avec une erreur relative d'environ 5 %. La précision de l'analyse est meilleure quand la quantité de nickel métallique est faible; la présence éventuelle de fer métallique ne gêne pas.

La méthode utilisant une solution de $HgCl_2$-KCN-HCl à pH 9 semble donner une précision un peu supérieure à celle obtenue par l'autre méthode, mais cet avantage est contrebalancé par une durée d'ébullition trois fois plus longue.

En conclusion, nous pouvons affirmer que la mise au point de ces deux méthodes nous a permis d'atteindre le but cherché.

RÉSUMÉ

Au cours de recherches sur le comportement du nickel métallique dans des milieux contenant $HgCl_2$, KCN et HCl, on a remarqué que dans certains cas, la dissolution de nickel métallique était complète, alors qu'un mélange d'oxydes de nickel restait absolument inaltéré.

Les conditions opératoires ont été précisées et les résultats ont permis de mettre au point deux méthodes de dosage du nickel métallique en présence d'oxydes de nickel dans des matières complexes, y compris des minerais.

Ces méthodes sont décrites en détail et les résultats d'essais sont donnés; ils montrent qu'on peut obtenir une précision d'environ 5 %.

SUMMARY

During investigations on the behaviour of metallic nickel in $HgCl_2$-, KCN- and HCl-containing media, it was noticed in certain cases that nickel metal dissolution was achieved, while a mixture of nickel oxides remained absolutely unaltered.

The working conditions were determined, and on the basis of the results obtained two methods have been developed for the determination of metallic nickel in the presence of nickel oxides in complex materials, including ores.

These methods are described in detail and the results of the experiments are given: they show that an accuracy of about 5 % can be obtained.

ZUSAMMENFASSUNG

Im Laufe der Untersuchungen über das Verhalten von metallischem Nickel in $HgCl_2$-, KCN- und HCl-haltigen Lösungen wurde bemerkt, dass in gewissen Fällen die Au lösung des metallischen Nickels vollständig war, während ein Nickeloxydgemisch ganz unverändert blieb.

Die Verfahrensbedingungen wurden genau bestimmt und die Ergebnisse haben erlaubt, zwei Analysemethoden des metallischen Nickels in Gegenwart von Nickeloxyden in komplizierten Stoffen, besonders in Erzen, aufzustellen.

Diese Methoden werden ausführlich beschrieben und die gefundenen Ergebnisse angeführt; sie zeigen dass eine Genauigkeit von 5 % erreicht werden kann.

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THE STORAGE OF SEA-WATER SAMPLES FOR THE DETERMINATION OF DISSOLVED INORGANIC PHOSPHATE

by

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A knowledge of the variation of the inorganic phosphate and total phosphorus content of sea-water is of considerable value to fishery chemists and marine biologists in the study of the fertility of the sea. In this connection several surveys of the phosphate concentration of surface waters and its relation to plankton and fish populations have been carried out. Although it is preferable to analyse sea-water samples immediately, this is not always possible. If such samples are stored without treatment, then the inorganic phosphate content of the water may be increased by the bacterial or enzymatic decomposition of the organic phosphorus of dead organisms, or decreased by its utilization by growing bacteria and plankton, or through adsorption on detritus.

A number of methods have been described for the preservation of sea-water samples for the determination of dissolved phosphate. IBANEZ[1] has recommended the addition of 1 ml of 1% sodium fluoride per 100 ml of sample. HARVEY[2] has suggested "baiting" the samples for determination of total phosphorus with freshly precipitated aluminium hydroxide, or preferably, with thorium carbonate, in an endeavour to adsorb epiphytic bacteria and organic matter so as to prevent them being adsorbed on the walls of the container; a few drops of chloroform were also added to prevent the proliferation of bacteria. The present work was carried out in an endeavour to find the optimum conditions for the preservation of samples to be analysed for inorganic phosphate.

EXPERIMENTAL

Samples of sea-water (chlorinity *ca.* $18.7\,^0/_{00}$) were filtered through a Whatman No. 1 filter paper, and then analysed for inorganic phosphate by HARVEY's molybdenum-blue method[2]. They were then stored in the dark at *ca.* 20° in 150 ml swing-top soda glass bottles after the addition of various preservatives. After 28 days the samples were again analysed for phosphate.

(1) *No preservative*

Two water samples (13.5 and 25.7 μg PO_4-P/l) were each stored in two bottles with no added preservative and, after 1 month were found to contain 15.7 and 15.6, and 28.2 and 29.2 μg PO_4-P/l respectively. This increase in the inorganic phosphate concentration is presumably due to bacterial or enzymatic hydrolysis of dissolved organic phosphorus compounds.

(2) *Sodium fluoride*

The fluoride ion inhibits the formation of molybdenum-blue. The addition of 1 ml and 2 ml of 1% sodium fluoride to 100 ml of sea-water containing 15 μg PO_4-P/l reduced the optical density of the molybdenum-blue (measured at 705 mμ) to 68.7% and 15.5% respectively of the optical density obtained in the absence of added fluoride. Since the presence of fluoride much reduces the sensitivity of the analytical method, the latter must be calibrated in the presence of the amount of fluoride used as a preservative. Three samples of sea-water (28.4 μg PO_4-P/l) to which 1 ml of sodium fluoride per 100 ml had been added, contained after one month, 23.0, 26.1 and 23.8 μg PO_4-P/l.

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(3) *Aluminium hydroxide and thorium carbonate*

Attempts to use either aluminium hydroxide or thorium carbonate (up to 10 mg/150 ml) for the preservation of water samples led to very high and variable results.

(4) *Chloroform*

Three samples of sea-water (28.4 μg PO_4-P/l) preserved by the addition of 1 ml of chloroform per 150 ml, contained after 1 month 28.1, 28.5 and 28.5 μg PO_4-P/l.

It thus appears that of the preservatives tested only chloroform was satisfactory, and its effectiveness has been confirmed by further experiments. It should be stressed that all the present work was carried out using filtered sea-water, and it is recommended that all samples should be filtered[4] immediately after collection. The specimens should be stored in the dark at as low a temperature as possible.

Use of polyethylene bottles for storage of sea-water samples

Polyethylene bottles are becoming quite widely used in oceanography for storage of water samples for silicate[4] and trace element determinations, since they are light, robust and free from the possibility of contamination by silicon or trace metals. They may also be used for the short period storage of water specimens for chlorinity determinations[5]. Experiments were therefore carried out to test the possibility of using water stored in polyethylene bottles for phosphate determinations, and it was found that their use led to the disappearance in less than 6 days of almost all the inorganic phosphate from the water. That this disappearance was due to the adsorption of the phosphate ion by the polyethylene was shown by the fact that a polyethylene sheet, which had been shaken with sea-water containing 500 μg PO_4-P/l, liberated considerable amounts of phosphate ion when shaken with several portions of distilled water.

CONCLUSIONS

Samples of sea-water to be analysed for inorganic phosphate should be filtered[4], and then stored in the dark after the addition of *ca.* 0.7 ml of chloroform per 100 ml of sample to inhibit bacterial action. Polyethylene bottles should not be used for the storage of samples to be analysed for phosphate since they adsorb phosphate ions strongly.

SUMMARY

A study has been made of methods of preservation of sea-water samples to be analysed for inorganic phosphate. It is recommended that the filtered samples be treated with 0.7 ml of chloroform per 100 ml of water and stored in the dark in glass bottles. Polyethylene bottles should not be used for water storage since they strongly adsorb phosphate ion.

RÉSUMÉ

Une étude a été effectuée sur les méthodes de préservation des échantillons d'eau de mer en vue de la détermination de leur teneur en phosphates inorganiques. Il est recommandé de traiter les échantillons filtrés par le chloroforme (0.7 ml $CHCl_3$ par 100 ml d'eau), et de les conserver dans l'obscurité dans des récipients en verre. Les flacons en polyéthylène ne doivent pas être utilisés pour la conservation de l'eau car ils adsorbent fortement les ions phosphoriques.

ZUSAMMENFASSUNG

Die Konservierungsmethoden von Meerwasserproben wurden im Hinblick auf die Bestimmung des Gehaltes an anorganischen Phosphaten untersucht. Es wird empfohlen die filtrierten Entnahmen mit Chloroform (0.7 ml $CHCl_3$ auf 100 ml Wasser) zu behandeln und sie in Glasgefässen im Dunkeln aufzubewahren. Polyäthylenflaschen dürfen für die Aufbewahrung des Wassers nicht verwendet werden, da sie die Phosphationen stark adsorbieren.

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ÉTUDES SUR LA DÉTECTION, LA CARACTÉRISATION ET LE DOSAGE DES ALDÉHYDES

I. MÉTHODES D'OXIMATION

par

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Parmi les méthodes proposées pour la détection et le dosage des aldéhydes, il faut sélectionner la ou les méthodes dont l'application semble être la plus universelle. Le réactif parfait serait celui qui précipiterait un aldéhyde quelconque, en formant un dérivé avec un point de fusion compris entre 50° et 200° par exemple, avec un rendement de 100 %, suffisamment stable pour être séché à poids constant. Un tel réactif permettrait à la fois la détection, la caractérisation et le dosage des aldéhydes.

Faute de ce réactif parfait, on peut essayer de trouver un composé, permettant par exemple le dosage par titrage, suivi de la séparation du dérivé obtenu, même si le rendement n'est pas de 100 %. L'oximation des aldéhydes a souvent été proposée. Ayant l'intention de faire une étude critique des diverses méthodes existantes, nous traiterons d'abord des méthodes d'oximation.

Parmi les procédés indiqués pour le dosage des aldéhydes par oximation, ceux recommandés par BRYANT ET SMITH[1], par WANKA, JUREČEK ET HOLÁNEK[2], par SMITH ET MITCHELL[3], par JOHNSTON[4] et par PERRET[5] semblent être les mieux étudiés et de la plus grande universalité.

On constate que certains radicaux liés au groupement aldéhyde peuvent gêner le dosage, en empêchant une réaction complète entre l'aldéhyde et l'hydroxylamine, ou en ralentissant considérablement la réaction.

Une oximation incomplète peut être due à un ,,empêchement stérique", causé par une ramification de la chaîne de carbone en position α par rapport au groupement aldéhydique. Un ralentissement de la vitesse de l'oximation peut être dû à la présence d'autres groupements dans la molécule, causant une déformation du système électronique du groupement aldéhyde.

Comme aldéhydes témoins, nous avons choisi les aldéhydes indiqués dans le Tableau I. Un empêchement stérique peut être prévu pour certains aldéhydes (I-IX), tandis que l'influence d'une déformation du système électronique peut être prévue parmi les numéros X-XIV.

Dans les Tableaux II et III, nous indiquons les poids moléculaires des aldéhydes examinés et les poids moléculaires que nous avons trouvés, en nous servant des 5 méthodes indiquées et en suivant les indications aussi rigoureusement que possible. D'après nos résultats, la méthode de SMITH ET BRYANT semble la plus universelle

TABLEAU I

ALDÉHYDES TÉMOINS POUR LES TITRATIONS

		Poids moléculaire
I.	Paraformaldéhyde	30.0
II.	Acétaldéhyde	44.0
III.	Aldéhyde isobutyrique	72.1
IV.	Aldéhyde triméthylacétique	86.1
V.	Heptaldéhyde	114.2
VI.	Benzaldéhyde	106.1
VII.	*o*-Tolualdéhyde	120.1
VIII.	*p*-Tolualdéhyde	120.1
IX.	2.6-Diméthylbenzaldéhyde	134.2
X.	Furfural	96.0
XI.	2-Thiofénaldéhyde	112.1
XII.	2-Pyridylaldéhyde	107.1
XIII.	3-Pyridylaldéhyde	107.1
XIV.	4-Pyridylaldéhyde	107.1

TABLEAU II

TITRATION DES ALDÉHYDES TÉMOINS D'APRÈS DES MÉTHODES DIFFÉRENTES D'OXIMATION

Aldéhyde témoin	*Méthode de* BRYANT ET SMITH		*Méthode de* WANKA, JUREČEK ET HOLÁNEK	*Méthode de* SMITH ET MITCHELL	*Méthode de* JOHNSTON
	Électrode de verre	*Électrode de platine*	*Électrode d'antimoine*	pH 2.5	pH 3.0
I	30.1	—	30.3	33	33.1
II	—	—	42.5	45.2	44.7
II*	46.7	—	—	—	—
III	—	—	78.8	73.6	72.3
III*	72.2	—	—	72.3	—
IV	100.7	—	132.8	132	126.3
V	113.0	109.4	153.3	125	—
V*	—	—	—	118.8	120.0
VI	108.8	106.2	—	109.7	107.8
VI*	105.8	—	107.8	105.1	—
VII*	124.5	120.5	132.0	125	131.9
VIII*	119	134	127.3	120.7	123.8
IX*	190.5	—	392	271	236
X*	94.8	100	93.9	97.2	97.4
XI	112.5	—	119.0	118	130.4
XII	103.5	—	—	104.5	146.2
XII*	109.6	108.2	—	—	—
XIII	105.8	—	—	—	—
XIV*	106.4	110.2	—	—	—

* fraîchement distillé

TABLEAU III

TITRATION DU BENZALDÉHYDE ET DU FURFURAL D'APRÈS LA MÉTHODE DE PERRET

Minutes de repos	*Poids moléculaires trouvés*	
	Benzaldéhyde	*Furfural*
30	107.4	108.8
60	107.5	97.6
90	108.6	98.2
120	108.8	96.4
180	—	116.2

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des méthodes examinées, mais même pour cette méthode nous avons trouvé des inexactitudes assez graves, dues partiellement à la détermination difficile du virage, le saut de potentiel n'étant pas suffisamment prononcé (voir Fig. 1).

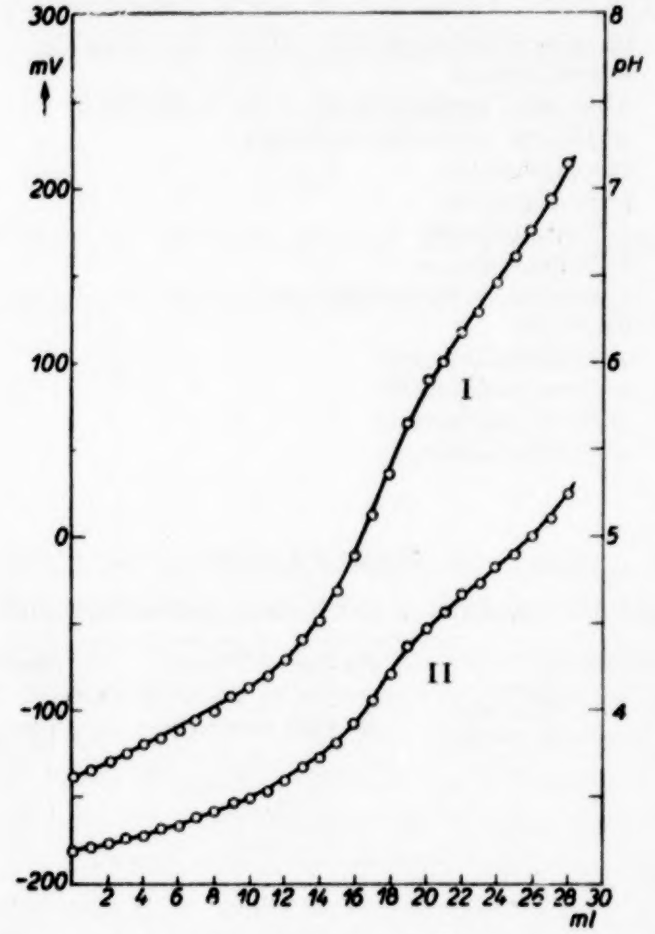

Fig. 1. Titration potentiométrique de l'oxime du furfural. Électrode de verre/Électrode au calomel
Courbe I: Ordonnée à droite (pH)
Courbe II: Ordonnée à gauche (mV).

Pour les méthodes où le point final de la titration est fixé au pH 2.5 ou pH 3.0, la présence dans la molécule d'un atome d'azote peut causer des inexactitudes (cas des pyridylaldéhydes) de même que la présence de l'hétéroatome soufre (2-thiofénaldéhyde).

Quelques inexactitudes correspondant aux déviations prévues par un empêchement stérique sont observées en comparant les numéros II, III et IV, et les numéros VI, VII, VIII et IX.

De plus, il faut s'assurer que les aldéhydes sont tout à fait purifiés des produits de polymérisation ou d'oxydation (peroxydes ou acides), deux déterminations faites avec un intervalle de 24 heures donnant souvent des différences de plusieurs %.

PARTIE EXPÉRIMENTALE

Méthode de Bryant et Smith[1]. Nous avons suivi les indications des auteurs, échangeant toutefois la bouteille à pression avec un gobelet, et fixant le temps de repos, après addition de l'aldéhyde au réactif, à 2 heures. La titration visuelle a été abandonnée pour une titration potentiométrique, utilisant le système électrode de verre — électrode au calomel, ou électrode de platine — électrode au calomel. Pour ce dernier système, la fixation du virage a été extrêmement difficile, même en appliquant les méthodes recommandées par Gran[6] ou par Sörensen[7]. Jensen[8], qui a comparé la méthode de Smith et Bryant avec une détermination par réduction avec le borohydride de sodium a eu les mêmes difficultés en fixant le virage (communication privée).

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Méthode de Wanka, Jureček et Holánek[2]. Nous n'avons examiné que la titration en solution aqueuse. La précision de cette méthode n'est pas suffisante. Quatre déterminations simultanées de l'aldéhyde isobutyrique ont eu un écart trop grand. La substitution de l'hydroxylamine libre au chlorhydrate d'hydroxylamine n'a pas donné des résultats plus satisfaisants.

Méthode de Smith et Mitchell[3]. Suivie rigoureusement, cette méthode nous a donné des résultats concordant avec les résultats indiqués par les auteurs. Un empêchement stérique est trouvé pour le triméthylacétaldéhyde, pour l'*o*-tolylaldéhyde et pour le 2,6-diméthylbenzaldéhyde. Une erreur causée par la présence d'un hétéroatome est trouvée pour le 2-thiofénaldéhyde et pour les pyridylaldéhydes, ces derniers étant trop basiques pour permettre une titration jusqu'au pH 2.5.

Méthode de Johnston[4]. Nous n'avons trouvé aucun avantage en substituant l'alcool butylique tertiaire à l'alcool éthylique.

Méthode de Perret[5]. Nous n'avons examiné que quelques-uns des aldéhydes, trouvant qu'il faut déterminer pour chaque aldéhyde le temps de repos nécessaire pour terminer l'oximation (voir Tableau III).

Oximes nouvelles

Parmi les oximes de nos aldéhydes témoins, il y en a trois que nous n'avons pas trouvé mentionnées dans la littérature et dont nous indiquons ici la préparation et les points de fusion.

Pour la préparation, nous nous sommes servis d'une méthode courante: 0.2 g de l'aldéhyde sont ajoutés à une solution de 0.5 g de chlorure d'hydroxylammonium dans 3 ml d'eau, puis 5-6 ml d'une solution de carbonate de sodium à 10 %. Le mélange est chauffé 10 minutes au bainmarie et refroidi dans l'eau glacée. Les oximes ne tardent pas à cristalliser, la cristallisation étant facilitée en grattant les parois avec une spatule. Ils sont ensuite recristallisés dans l'eau.

Dans le Tableau IV, nous indiquons les points de fusion et les analyses des oximes des pyridylaldéhydes −3 et −4 et de la 2,6-diméthylbenzaldéhyde.

En préparant l'oxime de la 4-pyridylaldéhyde, nous avons obtenu deux modifications avec les points de fusion 121-122° et 133-133.5°. La modification à point de fusion le plus élevé représente la forme stable.

TABLEAU IV

POINTS DE FUSION ET ANALYSES DE QUELQUES OXIMES

Oxime de	*Point de fusion*		%C	%H	%N *)
3-Pyridylaldéhyde	146−146.5°	calculé	59.00	4.95	22.94
		trouvé	58.90	4.82	22.36
4-Pyridylaldéhyde	133−133.5°	calculé	59.00	4.95	22.94
		trouvé	59.20	4.95	22.70
	121−122°	calculé	59.00	4.95	22.94
		trouvé	59.30	5.07	22.40
2.6-Diméthylbenzaldéhyde	158−159°	calculé	72.45	7.43	9.39
		trouvé	72.25	7.56	9.44

*) Microanalyses par M. Preben Hansen, Laboratoire de l'Université de Copenhague.

Pour examiner s'il s'agit des formes *syn* et *anti* de l'oxime nous avons, d'après les indications de A. Hantzsch[9], traité les deux oximes par l'anhydride acétique froid, puis par une solution froide de carbonate de sodium. La solution alcaline est extraite par l'éther, la couche éthérée est séparée et le solvant est évaporé. Le résidu est recristallisé dans l'essence de pétrole (point d'ébullition 60−100°). Les deux modifications ont donné une substance avec point de fusion 95−96°, que nous considérons comme l'acétate du 4-pyridylaldoxime:

$C_8H_8N_2O_2$	calculé	C 58.53 %,	H 4.91 %,	N 17.07 %
164.2	trouvé	C 59.15 %,	H 5.21 %,	N 17.22 %

L'acétylation semble être plus nette pour la substance avec point de fusion 133° que pour l'autre substance. Généralement c'est la forme *syn* qu'on peut acétyler, et l'expérience tend à indiquer, que les deux formes isolées sont des formes polymorphes, n'excluant tout de même pas complètement la possibilité d'une isomérie géométrique.

REMERCIEMENTS

Nous tenons à remercier Statens almindelige Videnskabsfond et Otto Monsteds Fond pour des bourses qui ont permis à l'un de nous de prendre part au travail.

RÉSUMÉ

On a comparé 5 méthodes pour le dosage des aldéhydes par oximation. Pour toutes les méthodes, une ramification simple ou double, en position *a* pour les aldéhydes aliphatiques et en positions 2 et 6 pour les aldéhydes aromatiques tend à diminuer la précision des méthodes (empêchement stérique).

Parmi les méthodes examinées celles de BRYANT ET SMITH[1] et de SMITH ET MITCHELL[3] sont les plus universelles.

Trois oximes nouvelles sont décrites. Pour l'une d'elles, deux modifications sont isolées, qui sont, toutes deux, transformées en acétate par l'action d'anhydride acétique et de carbonate de sodium. On discute s'il s'agit des formes *syn* et *anti* de l'oxime ou de deux modifications polymorphes.

SUMMARY

Five methods for the estimation of aldehydes by oximation have been compared. In all the methods, a single or double branching in position *a* in the case of aliphatic aldehydes, and in positions 2 and 6 in the case of aromatic aldehydes, tends to lessen the accuracy (steric hindrance). Of the methods examined those of BRYANT AND SMITH[1] and SMITH AND MITCHELL[3] are the most common.

Three new oximes are described. For one of these, two modifications have been isolated, both of which are converted to acetate by the action of acetic anhydride and sodium carbonate. The question is discussed whether this is a case of the *syn* and *anti* forms of the oxime or of two polymorphic modifications.

ZUSAMMENFASSUNG

Es wurden 5 Methoden für die Bestimmung von Aldehyden durch Oximation verglichen. Für alle diese Methoden wirken Verzweigungen der Moleküle im Sinne einer Verminderung der Präzision (sterische Hinderung), und zwar eine einfache oder doppelte Verzweigung in *a*-Stellung für aliphatische Aldehyde und in 2 und 6 Stellung für die aromatischen Aldehyde. Von allen diesen geprüften Methoden sind die von BRYANT UND SMITH[1] und von SMITH UND MITCHELL[3] die allgemeinsten.

Es werden drei neue Oxime beschrieben. Für eines von diesen wurden zwei Modifikationen isoliert, welche beide unter dem Einfluss von Essigsäureanhydrid und Natriumkarbonat in Acetate verwandelt werden. Die Frage wird erörtert ob es sich um die *syn*- und *anti*-Formen des Oximes oder um 2 polymorphe Modifikationen handelt.

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COMMENTS ON A MODIFIED TUTWILER METHOD FOR THE DETERMINATION OF H_2S AND SO_2 IN GASES

by

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INTRODUCTION

For controlling the operation of the well-known Claus sulphur recovery process, in which sulphur is obtained by the oxidation of hydrogen sulphide, a rapid method for analysing gases containing both H_2S and SO_2 is required.

Some years ago, a publication[1] appeared in which it was stated that the analysis could be carried out by a modification of Tutwiler's method[2] for determining H_2S. Since this modified form of the Tutwiler analysis has been adopted in industry, and the present author had occasion to find that its results are not reliable, this paper aims at showing its range of suitability and its shortcomings. At the end of the article reference will be made to an alternative analytical procedure developed by the author for carrying out this analysis.

The modified Tutwiler method consists in a titration of the total quantity of H_2S and SO_2 in a measured volume of gas with a standard iodine solution, in the presence of a neutral starch solution. This iodometric titration is followed by an acidimetric titration of the resulting hydriodic and sulphuric acids.

The simplicity of the method makes it particularly attractive for routine determinations. However, it is common knowledge that in aqueous media H_2S may react with SO_2 to form elementary sulphur and this reaction may also take place during the above determination. In order to investigate whether this method can nevertheless be used for the object in view, the experiments described below were carried out.

EXPERIMENTAL

When the Tutwiler method was employed for mixtures of *H_2S in nitrogen*, correct results were obtained in the iodometric titration. The acidimetric titration of the HI formed, however, gives low values (see Table I). This is probably due to oxidation of the HI.

When the Tutwiler method was applied to mixtures of *SO_2 in nitrogen*, both iodometric and acidimetric titrations gave low results. This fact is to be attributed to the loss of SO_2 during the introduction of the sample in the pipette, by solution in the outflowing starch solution. This is proved by the influence of the rate at which the starch solution is withdrawn from the pipette (see Table II, experiments 10 to 16).

TABLE I

ANALYSIS OF H_2S/N_2 MIXTURES

Gas Sample	*Expt. No.*	*Actual H_2S, % vol.*	*Experimental H_2S, % vol.*			
			iodometric		*acidimetric*	
			% vol.	*difference*	*% vol.*	*difference*
I	1	17.40	17.00	−0.40	not determined	
	2	17.40	17.20	−0.20	16.20	−1.20
	3	17.40	17.50	+0.10	16.65	−0.75
	4	17.40	17.40	0.0	16.60	−0.80
	5	17.40	17.70	+0.30	14.50	−2.90
	6	17.40	17.80	+0.40	16.80	−0.60
	average	17.40	17.43	+0.03	16.15	−1.25
II	7	4.96	4.85	−0.11	4.69	−0.27
	8	4.96	4.82	−0.14	4.33	−0.63
	9	4.96	4.72	−0.24	4.57	−0.39
	average	4.96	4.80	−0.16	4.53	−0.43

TABLE II

ANALYSIS OF AN SO_2/N_2 MIXTURE

Expt. No.	*Actual SO_2 % vol.*	*Kerosine layer*	*Rate of withdrawal of starch solution*	*Experimental SO_2, % vol.*			
				iodometric		*acidimetric*	
				% vol.	*difference*	*% vol.*	*difference*
10	3.95	without	slow	2.61	−1.34	2.65	−1.30
11	3.95	,,	moderate	3.16	−0.79	not determined	
12	3.95	,,	,,	3.04	−0.91	3.05	−0.90
13	3.95	,,	,,	2.98	−0.97	2.82	−1.13
14	3.95	,,	,,	3.32	−0.63	3.32	−0.63
15	3.95	,,	,,	3.20	−0.75	3.22	−0.73
16	3.95	,,	fast	3.62	−0.33	3.63	−0.32
17	3.95	with	slow	3.89	−0.06	3.71	−0.24
18	3.95	,,	moderate	3.95	0.0	not determined	
19	3.95	,,	,,	3.96	+0.01	3.87	−0.08
20	3.95	,,	,,	3.83	−0.12	3.95	0.0
21	3.95	,,	fast	3.92	−0.03	3.83	−0.12

A considerable improvement was effected by placing a thin layer of kerosine on the starch solution, so as to reduce the rate of solution of SO_2 in the starch solution (see Table II, experiments 17 to 21).

Gases containing both *H_2S and SO_2 in nitrogen* gave very erratic results (see Table III). A considerable amount of elementary sulphur was formed during the introduction of the gas as a result of the reaction between H_2S and SO_2, even when employing a kerosine layer on the starch solution.

An attempt was then made to eliminate the use of aqueous solution as confining liquid during the sampling. An evacuated dry pipette was filled with gas, whereupon a measured quantity of the standard iodine solution was admitted and the excess was titrated back in the liquid, after withdrawing the latter from the pipette, with sodium thiosulphate. Though this procedure led to better results (see experiments 28 to 30), it is less simple and consequently unattractive.

Summarizing, we can state that the modified Tutwiler method can be used for the determination of H_2S or of SO_2 alone, but not for gases containing both components.

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TABLE III

ANALYSIS OF AN $H_2S/SO_2/N_2$ MIXTURE

Expt. No.	Procedure	Actual H_2S % vol.	Actual SO_2 % vol.	H_2S found experimentally		SO_2 found experimentally	
				% vol.	Diff.	% vol.	Diff.
22	with kerosine film	2.40	4.21	0.72	−1.68	2.71	−1.50
23	,,	2.40	4.21	0.75	−1.65	3.02	−1.19
24	,,	2.40	4.21	0.84	−1.56	3.38	−0.83
25	,,	2.40	4.21	0.41	−1.99	3.34	−0.87
26	,,	2.40	4.21	0.78	−1.62	3.33	−0.88
27	,,	2.40	4.21	1.29	−1.11	3.48	−0.73
28	dry pipette	2.40	4.21	2.43	+0.03	4.51	+0.30
29	,,	2.40	4.21	2.11	−0.29	4.49	+0.28
30	,,	2.40	4.21	1.95	−0.45	4.57	+0.36

The present author, together with F. VAN DE CRAATS, recently published[3] another analytical method for the same purpose, which does not suffer from the above-mentioned disadvantages. It is based on the selective oxidation of H_2S and SO_2 in H_2O_2 solutions.

The gas to be analysed is passed through two washing-bottles, one filled with a neutral (or slightly acid) and one with an alkaline H_2O_2 solution. The SO_2 is oxidized in the former solution, the H_2S in the latter. The separation between the gases is completed by stripping the solutions with air. Subsequently the sulphuric acid formed in each washing bottle is titrated to the methyl red end-point.

Some determinations by the latter method on a synthetic mixture of H_2S, SO_2 and N_2 are given in Table IV.

TABLE IV

ANALYSIS OF A MIXTURE OF H_2S (2.10% VOL.), SO_2 (4.40% VOL.) AND N_2 (REMAINDER) BY THE H_2O_2 METHOD[3].

H_2S (% vol.)		SO_2 (% vol.)	
Found	Diff.	Found	Diff.
2.15	+0.05	4.43	+0.03
2.10	—	4.27	−0.13
2.10	—	4.38	−0.02
2.13	+0.03	4.42	+0.02

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SUMMARY

A modified form of the Tutwiler analysis which was proposed a few years ago and has to some extent, been used as a method for controlling the Claus sulphur recovery process, has been examined as to its exactitude for this purpose, *viz.*, for determining both H_2S and SO_2 in gas mixtures.

It has been found suitable for the determination of H_2S alone, and also (with a small modification) of SO_2 alone, but not for both compounds if they occur together.

These disadvantages are not possessed by an alternative method of analysis, recently published.

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RÉSUMÉ

Une forme modifiée de l'analyse selon Tutwiler a été proposée il y a quelques années et employée dans quelques cas isolés pour le contrôle du procédé Claus de récupération du soufre. Une étude a été faite pour en examiner le degré d'exactitude dans cette application, c.à.d. pour la détermination de H_2S et de SO_2 dans des mélanges gazeux.

Il a été trouvé que la méthode se prête bien à la détermination de H_2S seul et, avec une légère modification, de SO_2 seul, mais non à celle des deux substances si elles sont présentes en même temps.

Une autre méthode d'analyse récemment publiée ne présente pas ce désavantage.

ZUSAMMENFASSUNG

Eine geänderte Form der Tutwiler Analyse, die vor einigen Jahren als Methode zur Kontrolle des Claus-Verfahrens zur Zurückgewinnung von Schwefel vorgeschlagen wurde und in einzelnen Fällen benutzt worden ist, wurde auf ihre Genauigkeit für diesen Zweck, d.h. für die Bestimmung von H_2S und SO_2 in Gasgemischen geprüft.

Es stellte sich heraus, dass die Analyse sich eignet zur Bestimmung von H_2S allein und (mit einer geringen Änderung) auch von SO_2 allein, aber nicht von beiden Verbindungen wenn sie gleichzeitig vorkommen.

Eine andere Analysenmethode, die neulich veröffentlicht wurde, hat diese Nachteile nicht.

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IMPEDANCE METHOD OF ZONE LOCALIZATION FOR PAPER CHROMATOGRAPHY WHICH OBVIATES THE NEED FOR PRELIMINARY SPRAYING

by

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In 1936 in connection with his work on conductimetric analysis and titration the writer showed that the difficulties due to polarization, adsorption, precipitation, cell cleaning, and electrode platinizing could be avoided by the employment of radio-frequencies which enable the electrodes to be separated from the solution and placed against the outside of a glass vessel containing the liquid. Since that date this device has come into general practice[20,21].

At first in 1936 the writer employed a heterodyne method for chemical analysis and measured variations in frequency caused by changes in solution concentration[1]. He followed this in 1944-1945 whith his Q-metric method again placing the electrodes on the outside of the glass tube which contained a sample of the solution[1-4].

In 1945 in conjunction with his rectified radio-frequency (R.Rf.) method of conductimetric analysis a similar tube fitted with external electrodes was employed[4]. This was followed in 1947 by his shielded "Conductimetric Tube"[5-8].

CHROMATOGRAPHIC ZONE LOCATION

The method for locating chromatographic zones described in the present paper again makes use of the same principles.

When operating at a fixed frequency the impedance of the solution or substance which separates the electrodes is dependent upon conductance and dielectric constant. When the conductance of the sample under test is high its dielectric constant will cause little or no appreciable effect. J. L. HALL and his associates[9,10] when discussing the operation of cells having external electrodes also draw attention to the fact that the meter measurements are a function of the conductance and dielectric constants of the solution and state that whatever the type of cell its conductance will vary in accordance with the resistance of the solution.

Titration graphs when plotted are actually portions of a radio-frequency impedance curve relatively so large that for practical purposes the short portion covered is almost indistinguishable from a linear graph.

Conductance plays the major part in determining the meter deflections. The same remark applies also to those obtained for chromatographic zones as located by the writer's earlier methods [1, 2], where the paper strips are sprayed with distilled water before localization.

CONSIDERATIONS

The filter paper used (on examination by the writer's moisture meter[16]) was found to be hydroscopic, and the idea occurred to him that matters might be arranged so that the chromatograph should make actual contact with the electrodes, and that under these conditions the zones might be sufficiently conductive after exposure to the air for a few hours. Were this to be so the necessity for spraying might be avoided[11,12].

It was also evident that the removal of the glass strips between which the chromatograph was sandwiched[11,12] would reduce the impedance of the circuit.

EXPERIMENTAL TESTS

Fig. 1 shows the circuits and arrangement of the electrodes used for the first tests.

E and E′ in this figure are two strips of metal foil which serve as electrodes, each is 16 cm long. They are attached to the adjacent edges of two sheets of glass (or better still polystyrene) G and G′ separated by an air gap about 2 mm wide. The radio-frequency current from an oscillator* regulated by means of a small coupling condenser C (0.00001 μF) is fed to electrode E. The second electrode E′ is connected to earth through a germanium rectifier Re in the R.Rf. circuit. When only air bridged the gap between the electrodes only a minute rectified current was registered. The meter deflection was then set back to zero by the zero-shunt and an unsprayed chromatograph was passed slowly across the gap carefully keeping it in contact with the electrodes. A meter reading of 10 μA was obtained for the filter paper between the zones, and very much larger readings for each zone according to its ionic concentration. These were quite comparable to the readings obtained for the same inorganic salts by the writer's original methods.

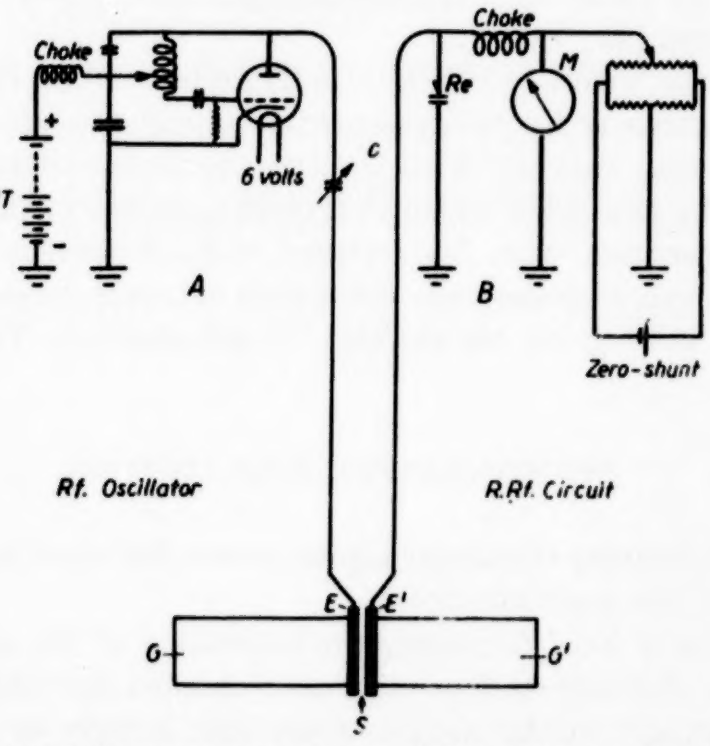

Fig. 1. A and B are circuit diagrams respectively of the oscillator and the rectifying circuits used in conjunction with BLAKE's "Doubled-electrode Zone Locater".

At this stage a difficulty was experienced — that of keeping the chromatograph evenly in contact with the electrodes as it was passed across the air gap S. Any uneven pressure or crinkling of the paper affected the meter readings. In the original methods[11,12] sandwiching the paper between glass strips avoided this difficulty. With unsprayed paper however the use of glass was not practicable as its presence caused too great an increase in capacitance.

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* Both the Hartley-Child oscillator and the R.Rf. circuits shown in the Figure are well known and have been described already[13].

Doubled electrodes

Eventually a solution was found. The design and size of the electrodes was altered, and "*doubled electrodes*" were employed. The instrument as designed will take chromatographs of any width up to 14 cm.

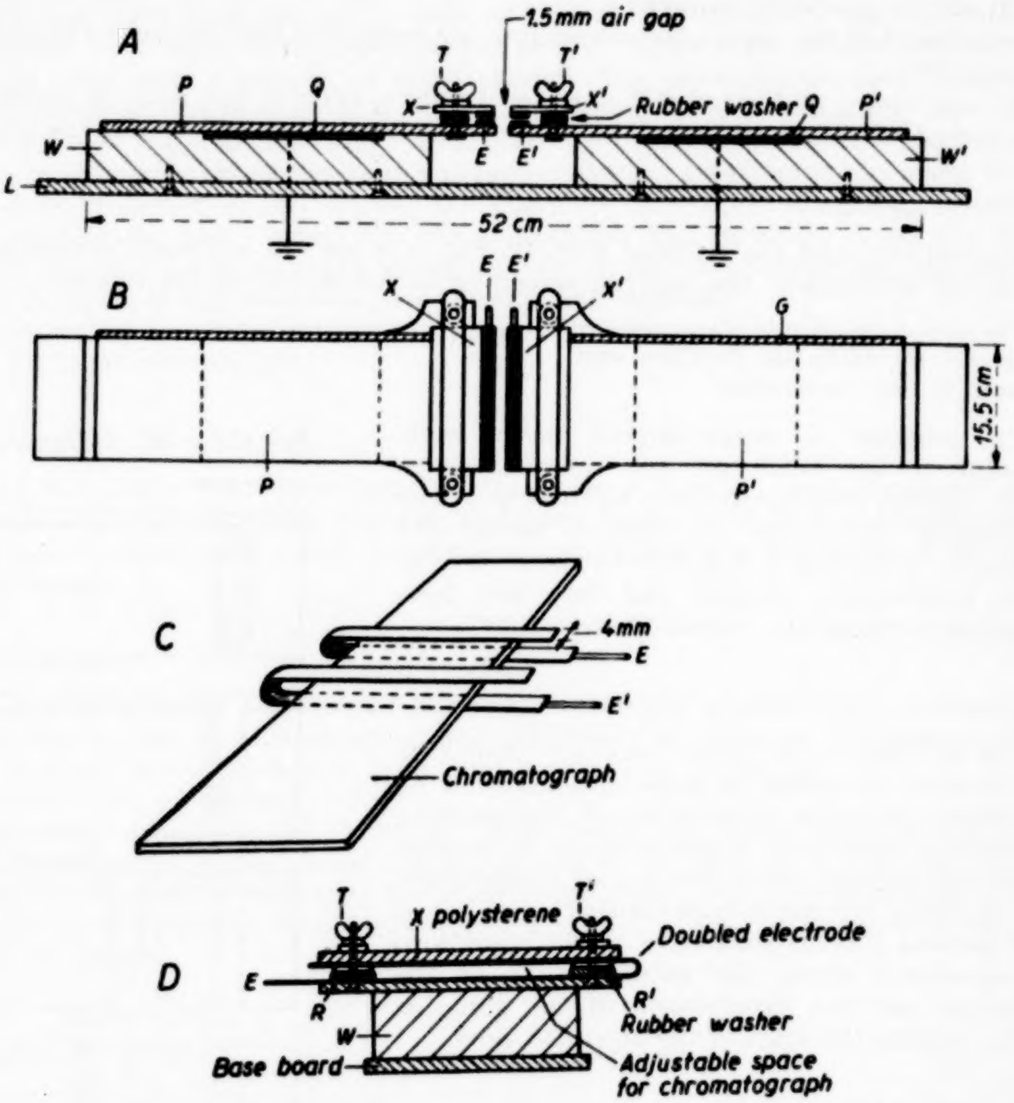

Fig. 2. A is a section of the Rf Zone Locater for conductive and non-conductive chromatographs. B shows the same instrument as viewed from above.
C illustrates the passage of a chromatograph through the two "Doubled-electrodes" E and E'.
D is the end view of the Zone Locater. In this diagram only one "Doubled-electrode" E is visible, the second electrode is behind it and out of sight.

Each of the two electrodes was formed by doubling over a strip of metal foil so that one half was exactly over the other as indicated in Fig. 2 C. During operation if no zone is present the space between the two halves of each electrode will always be occupied by the same total amount of air and paper (*i.e., the dielectric constant will remain unchanged*), therefore when the chromatograph is repeatedly passed across the gap between two such doubled electrodes the same deflections are obtained every time for each zone.

Doubled electrode R.Rf. chromatographic zone locater

The presence of a minute quantity of water picked up hydroscopically adds greatly to the conductivity of the chromatographs.

The construction of the zone locater is seen in Fig. 2 A which is a sectional sketch. Fig. 2 B shows the zone locater as viewed from above. P and P' are two sheets of 3 mm polystyrene each 15.5 cm wide except at their ends where the electrodes are attached, here they are widened sufficiently to allow for holes to be drilled to take the bolts and thumbscrews by means of which two strips of polystyrene X and X' are clamped in position. The upper halves of the electrodes E and E' are attached to the under surfaces of X and X', and their lower halves are fastened to the upper surface of P and P'.

The space between the surfaces of the electrodes (through which the chromatograph travels) is kept open by means of rubber washers and can be set to accord nicely with the thickness of the paper by four thumbscrews, only two of which T and T′ are seen in the sketches. Fig. 2 D is a sectional end view showing X in position over the polystyrene sheet P.

As the thumbscrews T and T′ are tightened the space between the upper and lower surfaces of the electrodes is gradually reduced.

It will be noted that the electrodes as mounted are supported well above the base L by wooden blocks W and W′.

Q and Q′ are metal plates connected to earth; these restrict the field on either side of the electrodes, and prevent the proximity of the operator's hands from influencing the meter readings.

Screened circuits and leads

Both the oscillator and the rectifier circuits, Fig. 1 A and B, are earth screened, as also are the leads to the electrodes. The earthed screening is not shown in the figures.

A technique for recording the position and measurements of zone intensities

For this purpose a micro-ampere meter scale (corresponding to the scale on the micro-ammeter in the R.Rf. circuit) may be attached to the top of one of the "doubled electrodes" E., Fig. 2. Before the chromatograph is localized it is covered by a strip of thin paper (typewriting paper) and they are both passed together through the "doubled electrodes".

Recording

The meter deflections for each zone are read first and then recorded according to scale measurement on the paper which covers the chromatograph. The marking (a series of dots) is made with a pencil which is inserted through the gap between the upper halves of electrodes E and E′, marking the cover paper where it lies across the gap. A general picture indicative of the variations in the impedance along the entire length of the chromatograph and the distribution of the zones is obtained by joining the ends of the recorded dots.

Sample chromatographs

Fig. 3 shows the plottings from a series of chromatographs. The gradual separation of $CuCl_2$ from KCl is seen over a period of five hours (solvent ethyl alcohol). On the actual chromatographs the shaded band was stained a light green by the $CuCl_2$.

The KCl zone being colourless was not visible but it is clearly revealed by localization. The maxima and minima of ionic intensity are sharply defined. It is interesting to note that the original zone which contained both the $CuCl_2$ and the KCl before development are completely cleared of those substances as development progresses. After 5 hours the two zones are seen still to overlap, obviously a much longer time would be required for them to separate completely.

Circuits

The circuits shown in Fig. 1 were those employed and were amply sensitive. However where zones containing much smaller quantities, or less conductive substances are to be localized, up to sevenfold amplification can be obtained by employing the writer's "Dual purpose transistor circuit"[14].

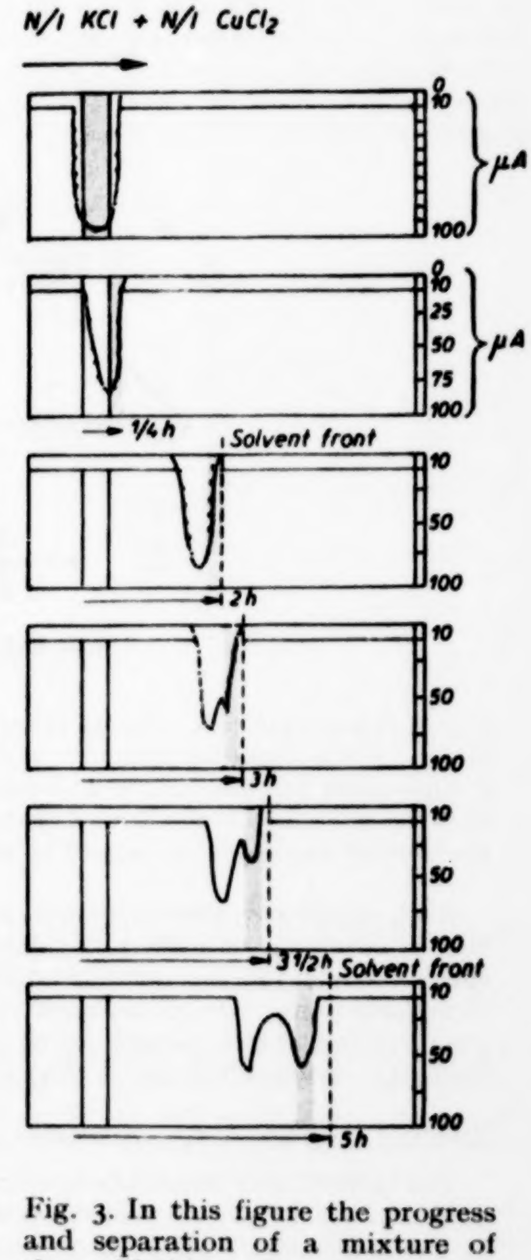

Fig. 3. In this figure the progress and separation of a mixture of the chlorides of copper and potassium is followed in a series of chromatographs over a period of five hours. The shaded band represents the faint green coloration of the $CuCl_2$.

Technique

Gravity fed chromatographs. The method followed in developing and preparing the chromatographs Fig. 3 was as follows:

Six strips of No. 1 Whatman's filter paper each 10.5 cm wide and 25 cm long were tested for uniformity by passing them across the localizer. After this a band 2 cm wide was marked by two pencil lines 5 cm from one end of each, and equal quantities of 1 mol KCl and $CuCl_2$ (0.02 cm) were applied over each band thus marked out[15,17]. They were then dried and suspended from a trough filled with a solvent of ethyl alcohol. The development took place in a closed developing chamber at the bottom of which (not touching the papers) there was a small quantity of equal parts of ethyl-alcohol and water, the evaporation from which kept the atmosphere saturated. As the temperature of the room was fairly constant no attempt was made to control it.

The container remained closed during the complete development of each chromatograph. When the desired time had elapsed the chromatograph was carefully dried and it was once more suspended over the ethyl-alcohol water mixture in the closed chamber and left there over night. In the morning it was ready to pass through the localizer.

For this test strong concentrations were employed in order that the green colour of the cupric chloride should be clearly visible.

Zone intensification

Experiment has shown that when only relatively weak solution concentrations are used for the chromatographs it is possible to intensify the zones temporarily by exposing them for twenty or thirty seconds to steam over a dish of boiling water. In this way the conductivity of the zones is greatly increased.

Dielectric comparisons

The following experiment was carried out with the simple arrangement of single electrodes already described in Fig. 1. This opens up the possibility of adapting the zone locater for the comparison of zones having dielectric (and semi-conductive) properties.

The experiment was as follows:

Samples of mica, rubber, paper of various thicknesses, and other materials some of which were partially conductive when placed across the electrodes each gave a distinctive meter deflection: It was of interest to note that the reading obtained for a small sample of window glass almost equalled that registered for a piece of metal of similar size separated from the electrodes by a sheet of dry paper.

NOTES AND SUGGESTIONS

As yet this work is in its early stages, doubtless many applications and variations in technique will be made. For example it may be possible to find some suitable substance with which to impregnate the paper before or after development in order to intensify the contrast between the conductance of the zones and the paper.

Up till now one of the difficulties encountered when distinguishing the solute contained in one zone from that in another zone has been the absence of any "exact mathematical point" or line[18] in any zone from which Rf measurements[17,18,19] could be made $\left(\mathrm{Rf} = \dfrac{\text{Rate of solute travel}}{\text{Rate of solvent travel}}\right)$.

The "Impedance" method of zone localization enables critical reference points to be located both for the regions of greatest density and for the edges of each zone. This method resembles the author's method for measuring the diffusion rate of liquids[22]. In both methods a region of given ionic density is selected as a point of reference which is then followed as it travels.

The following Rf values were obtained for metallic chlorides from "spot" chromatographs on No. 1 Whatman filter strips 2.5 cm wide (solvent *n*-butanol saturated with 3*N* HCl). After ascending development the chromatographs were hung up to dry over night and the measurements were made the next morning by means of the "Doubled-electrode Zone Locater".

	Time of development	*Rf Value*
Cu	1 h	0.210
	2 h	0.211
	3 h	0.215
Hg	3 h	0.813
A mixture of	3 h	Cu 0.222 and Hg 0.806
Cu and Hg	5¼ h	Cu 0.210 Hg 0.812

QUANTITATIVE ESTIMATIONS

With further reference to Fig. 3 the sharp definition of the areas containing the various solutes suggests the possibility of developing a technique for quantitative measurements.

Further work is proceeding with this object in view.

SUMMARY

In 1936, BLAKE suggested and then applied radio-frequency currents to chemical analysis. He demonstrated that when a Rf current pulses through a solution from which the electrodes are separated by an insulator the impedance of the circuit is comparable to that of a condenser bridged by a resistance. The author again makes use of such a circuit in his radio-frequency zone locater for paper chromatographs. Details of the circuits are given together with illustrative diagrams. A feature of this method is that the need for spraying the chromatographs is obviated. It is also suggested that a technique for quantitative measurement of the contents of each zone may be developped.

RÉSUMÉ

En 1936, BLAKE proposa l'application des courants de radio-fréquence à l'analyse chimique. Il démontra que lorsqu'un courant de radio-fréquence traverse une solution dans laquelle les électrodes sont séparées par un isolant, l'impédance du circuit peut être comparée à celle d'une capacité pontée par une résistance. L'auteur utilise un tel circuit pour détecter par radio-fréquence les zones des chromatogrammes sur papier. Les détails des circuits sont donnés, illustrés par des diagrammes. Cette méthode permet d'éviter de révéler les chromatogrammes. On se propose également de développer une technique d'analyse quantitative pour chaque zone.

ZUSAMMENFASSUNG

1936 schlug BLAKE die Anwendung der Radiofrequenz-Ströme für die chemische Analyse vor. Er zeigte, dass wenn ein Radiofrequenz-Strom durch eine Lösung geht, in welcher die Elektroden durch eine Isolation getrennt sind, die Impedanz des Stromkreises verglichen werden kann mit derjenigen, welche eine mit einem Widerstand verbrückte Kapazität aufweist. Der Autor verwendet einen solchen Stromkreis, um mit Radiofrequenz die Zonen der Papierchromatogramme aufzuzeigen. Die Einzelheiten der Stromkreise werden gegeben und durch Diagramme veranschaulicht. Diese Methode erlaubt die Entwicklung der Chromatogramme zu umgehen. Man beabsichtigt auch eine Technik zu entwickeln, welche die quantitative Analyse für jede Zone ermöglicht.

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PAPER CHROMATOGRAPHY OF FATTY ACIDS AND HALOGENATED ORGANIC ACIDS

by

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A paper chromatographic method is described for the separation and analysis of the volatile fatty acids and some halogenated organic acids. This was developed in order to identify certain acids formed in small quantities during the base-catalysed halogenation of aliphatic ketones[1].

EXPERIMENTAL

Apparatus and procedure

Whatman's No. 4 filter paper was used throughout, and the developing solvent contained 70% propanol and 30% concentrated ammonia[2]. The quantity of acid on the paper should not exceed 50-100 μg, as greater amounts give elongated spots on development, which makes it difficult to determine the R_F value accurately[3,4]. A development time of about 18 hours was generally sufficient, the solvent reaching the bottom of the paper in about 20 hours.

Materials

Commercial samples of the acids were used whenever obtainable, and these were purified by conventional methods.

α-Bromo-propionic acid was prepared by direct bromination of propionic acid in presence of phosphorus trichloride and was purified by distillation under reduced pressure[5].

With the exception of iodoacetic acid and β-iodo-propionic acid, of which commercial samples were available, the iodo-acids were prepared in small yield by refluxing the corresponding bromo-acids with potassium iodide in acetone[6] and were purified by recrystallization from petroleum ether.

The acids were dissolved in dilute aqueous ammonia, and the resulting solutions of their ammonium salts were applied to the chromatograms.

Spraying reagents

The following reagents were used to locate the positions of the acids:

1. *Fatty acids.* The chromatograms were sprayed with a slightly alkaline solution of B.D.H. Universal Indicator (pH adjusted to 9.5)[7]; this avoids the necessity of maintaining a carbon dioxide-free atmosphere, which has to be used when thymol blue is the spraying reagent[2]. Acids on the paper appeared as red spots on a blue background. The halogenated acids are also visible, but these can be distinguished from the unsubstituted acids by the procedures given below.

2. *Iodo-acids.* The developed chromatograms were allowed to hang for 5-10 seconds in a glass tank filled with dilute gaseous chlorine. The positions of the acids are visible as yellow spots on a white background. Chlorine liberates iodine from the iodo-acids, which reacts with ammonia (already present in the paper from the developing solvent) to give a "stain" due to formation of nitrogen iodides.

3. *Bromo-acids.* The chromatograms were sprayed with an 0.1% solution of fluorescein in 75% v/v aqueous ethanol, and the paper strips were then allowed to hang for about 5 seconds in a chlorine tank. The liberated bromine reacts with fluorescein on the paper and red spots, due to the formation of eosin, are visible on an almost white background, indicating the positions of the bromo-acids.

An 0.1% solution of α-naphthoflavone in acetone was also used as a spraying reagent, and the positions of the bromo-acids are then visible as orange-yellow spots. This reagent was not, however, as sensitive as fluorescein.

4. *Mixtures of bromo- and iodo-acids.* The chromatograms were sprayed with 0.1% fluorescein solution and were then allowed to hang for a few seconds in a chlorine tank. The bromo-acids are visible as red spots and the iodo-acids as intense yellow spots on an almost white background.

RESULTS

The method was standardized with solutions of some pure lower fatty acids and their bromo- and iodo-derivatives, and the R_F values of these acids are given in Table I. All results are average values for determinations carried out in triplicate;

TABLE I

R_F VALUES OF SOME LOWER FATTY ACIDS AND THEIR BROMO- AND IODO-DERIVATIVES

Acid	*R_F value*	*Acid*	*R_F value*	*Acid*	*R_F value*
$HCOOH$	0.38 (0.37)				
$CH_3.COOH$	0.39 (0.37)	$CH_2.Br.COOH$	0.45	$CH_2I.COOH$	0.50
$CH_3.CH_2.COOH$	0.48 (0.48)	$CH_3.CHBr.COOH$	0.52	$CH_3.CHI.COOH$	0.55
		$CH_2Br.CH_2.COOH$	0.52	$CH_2I.CH_2.COOH$	0.56
$CH_3.CH_2.CH_2.COOH$	0.57 (0.57)	$CH_3.CH_2.CHBr.COOH$	0.60	$CH_3.CH_2.CHI.COOH$	0.62
$(CH_3)_2.CH.COOH$	0.57 (0.57)	$(CH_3)_2CBr.COOH$	0.61	$(CH_3)_2CI.COOH$	0.63
$CH_3.CH_2.CH_2.CH_2.COOH$	0.68 (0.69)	$CH_3.(CH_2)_2.CHBr.COOH$	0.70	$(CH_3)_2CH.CHI.COOH$	0.72
$(CH_3)_3C.COOH$	0.70 (—)	$(CH_3)_2CH.CHBr.COOH$	0.70		

The figures in brackets are the corresponding R_F values of the fatty acids determined by ISHERWOOD AND HANES[6].

TABLE II

PAPER CHROMATOGRAPHIC SEPARATION OF MIXTURES OF LOWER FATTY ACIDS AND THEIR BROMO- AND IODO-DERIVATIVES

Components present	*R_F values*		
	1st Component	*2nd Component*	*3rd Component*
$CH_3.COOH$, $CH_2I.COOH$	0.39 (0.39)	0.50 (0.50)	—
$CH_3.COOH$, $CH_3.CH_2.CH_2.COOH$	0.39 (0.39)	0.56 (0.57)	—
$CH_2Br.COOH$, $CH_2I.COOH$	0.44 (0.45)	0.50 (0.50)	—
$CH_2I.COOH$, $CH_2I.CH_2.COOH$	0.49 (0.50)	0.55 (0.56)	—
$CH_2I.COOH$, $CH_3.CH_2.CHBr.COOH$	0.50 (0.50)	0.61 (0.60)	—
$CH_2I.COOH$, $CH_3.CH_2.CH_2.COOH$, $CH_3.CH_2.CH_2.CHBr.COOH$	0.50 (0.50)	0.55 (0.57)	0.69 (0.70)
$CH_3.COOH$, $CH_2Br.COOH$, $CH_3.CH_2.CHBr.COOH$	0.37 (0.39)	0.46 (0.45)	0.60 (0.60)
$CH_2Br.COOH$, $CH_2I.COOH$, $CH_3.CH_2.CH_2.CHBr.COOH$	0.45 (0.45)	0.51 (0.50)	0.69 (0.70)

The figures in brackets are the corresponding R_F values of the acids determined in blank runs (*cf.* Table I).

individual determinations varied from the mean value by not more than 2%. For the fatty acids, the R_F values are in good agreement with those found by ISHERWOOD AND HANES[6].

In Table II are given some typical results obtained on chromatographic analysis of mixtures of fatty acids and halogenated organic acids, and it will be seen that the R_F values of all the compounds studied are unaffected by the presence of other components. In general, the R_F values appear to be largely a function of molecular weight, and isomeric compounds have the same R_F value.

ACKNOWLEDGEMENT

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SUMMARY

A paper chromatographic method is described for the identification of the volatile fatty acids and some of their bromo- and iodo-derivatives. Some new spraying reagents are suggested which enable the different classes of acids to be detected in presence of one another.

RÉSUMÉ

Une méthode chromatographique sur papier est décrite pour l'identification des acides gras volatils et quelques-uns de leurs bromo- et iodo-dérivés. Quelques réactifs révélateurs sont proposés pour permettre de déceler les différentes catégories d'acides en présence les unes des autres.

ZUSAMMENFASSUNG

Eine papierchromatographische Methode zur Identifizierung von flüchtigen Fettsäuren und einigen ihrer Brom- und Jodderivate wird beschrieben. Einige neue Entwicklungsreagenzien werden vorgeschlagen, die erlauben sollen, die verschiedenen Klassen von Säuren nebeneinander zu erkennen.

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A PRECISE, DIRECT, HETEROMETRIC MICRO-DETERMINATION OF MERCURY WITH DIETHYLDITHIOCARBAMATE IN EXCESSES OF METALS

ETHYLENEDIAMINETETRAACETATE SOLUTIONS

by

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INTRODUCTION

In a previous investigation[1] we showed that tenths of a mg of mercuric mercury or of diethyldithiocarbamic acid (CBM) in 20 ml solution, could be determined heterometrically with either CBM or mercuric nitrate, with an error of 0-2%. At room temperature the titration takes about half an hour.

In this paper further results are presented which were obtained in the presence of complexing agents, chiefly a strong ammoniated solution of ethylenediaminetetraacetate (= EDTA). The investigation was restricted to the use of dilute solutions of the latter and therefore the amount of foreign metal present was accordingly reduced. But as EDTA did not interfere with the main reaction, the amount of EDTA in the strong ammoniated solution could have been many times greater under these conditions. Consequently, the amount of the foreign metal which could be retained in solution, to give a complex with EDTA, could have been many times greater than that used in these experiments.

EXPERIMENTAL

The same apparatus and the same technique were used as in the previous heterometric investigation. 20 ml solution was used. The reaction vessel had a diameter of 4 cm. The titrations lasted ∿30 minutes. Only in the case of copper, a green filter was tried but the results were not improved. Both the Na_2H_2EDTA and the Na-diethyldithiocarbamate were pure and were Eastman products. The mercuric nitrate was a crystallised reagent $Hg(NO_3)_2.H_2O$ by Baker and Adamson.

The end-points were obtained from enlarged curves, by the intersection of the line of the last part of the titration curve with the horizontal maximum optical density line.

RESULTS

The composition and results of a selection of experiments are given in Table I. Selected experiments are presented in Figs. 1 and 2 (the same numeration is used in the table and in the figures).

In all cases, with the exception of copper, the first maximum optical density point was reached at the calculated end-point of the quantitative formation of Hg(CBM)$_2$. In most cases the error was nearly zero, although in particular cases it was as high as 2.2%.

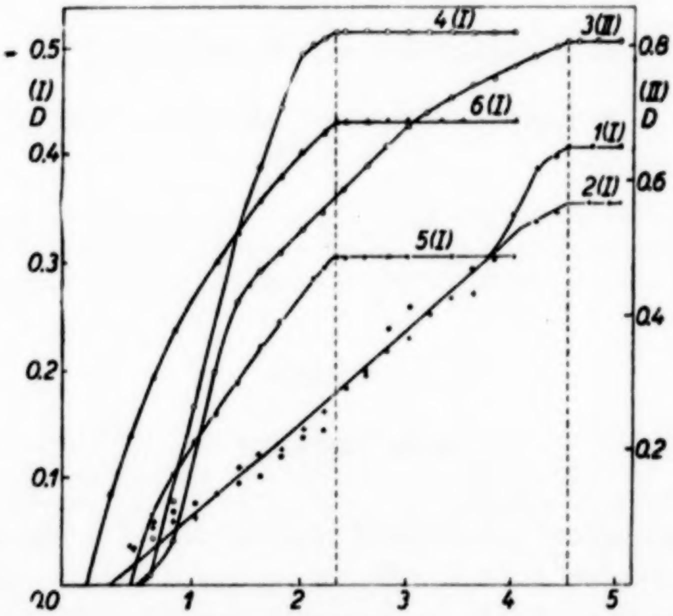

Fig. 1. The precipitation of mercuric carbamate in the presence of complexing agents.

Titrations in the presence of complexing agents

Fig. 1 presents the results obtained in the presence of different complexing agents, but in the absence of foreign metals. In the presence of pyro- and tripolyphosphate (curves 1 and 2) disturbances occured during the titrations, but the end-point was clear. Smooth titrations occurred in the presence of strong ammoniated citric acid (curve 6) or EDTA. In the presence of the latter, the maximum density values obtained were proportional to the amount of mercury which was titrated (curves 3-5). This is probably due to the gradual precipitation of mercury which formed a complex with EDTA and to the formation of final uniform particles of Hg(CBM)$_2$. It is interesting to note that in curve 3, Fig. 1 intermediate breaks may be discerned in addition to the final compound of Hg(CBM)$_2$.

Titrations in the presence of foreign metals

Table I shows the composition of the experiments and the results obtained. In all cases the molar ratios of mercury to the foreign metal were either 1 : 17 or 1 : 33. In no case did the presence of the foreign metal appreciably change the maximum optical density value as compared to the blank. In the case of copper alone, no constant maximum density line was reached and the densities increased continuously. In the presence of silver no precipitation occured. With chromium a precipitation appeared before the beginning of the titration.

TABLE I

General composition: 3 ml $Hg(NO_3)_2$ a*M* + *K* ml supplements + (17-*K*) ml H_2O + *x* ml diethyldithiocarbamate (= CBM) b*M*. Temp. 20°

Expt. nos.	*Solution*	*Molarity of* $Hg(NO_3)_2$ *(a)*	*Molarity of CBM (b)*	*Found CBM x ml*	*Maxim. density value*	*Initial precip. at ml*	*Titration time (min)*	*Theoretical point at ml*	*% error*
1	1 ml $Na_4P_2O_7$ 0.125*M*	0.002	0.0028	4.45	0.41	0.4	60	4.5	−1.1
2	1 ,, $Na_5P_3O_{10}$ 0.2 ,,	0.002	0.0028	4.50	0.36	0.4	40	4.5	0.0
3	4 ,, Na_2H_2EDTA 0.05*M* + 2 ml NH_3 2*M*	0.002	0.0028	4.45	0.80	0.6	30	4.5	−1.1
4	4 ,, ,, ,, + 2 ,, ,, ,,	0.001	0.0028	2.30	0.52	0.6	40	2.25	+2.2
5	4 ,, ,, ,, + 2 ,, ,, ,,	0.0005	0.0014	2.30	0.30	0.6	45	2.25	+2.2
6	1 ,, Na_3-citrate*M* + 2 ,, ,, ,,	0.001	0.0028	2,25	0.43	0.2	25	2.25	0.0
7	2 ,, Na-acetate 0.1*M*	0.002	0.0028	4.50	0.70	1.6	15	4.5	0.0
8	1 ,, CH_3COOH *M*	0.002	0.0028	4.45	0.85	2.8	30	4.5	−1.1
9	1 ,, ,, ,,	0.0005	0.0014	2.25	0.29	1.2	20	2.25	0.0
10	4 ,, Na_2H_2EDTA 0.05*M* + 2 ml NH_3 2*M* + 1 ml $Bi(NO_3)_3$ 0.1*M*	0.002	0.0028	4.45	0.80	0.6	30	4.5	−1.1
11	4 ,, ,, ,, + 2 ,, ,, ,, + 1 ,, ,, ,,	0.001	0.0028	2.25	0.53	0.4	35	2.25	0.0
12	4 ,, ,, ,, + 2 ,, ,, ,, + 1 ,, ,, ,,	0.0005	0.0014	2.18	0.27	0.6	35	2.25	
13	4 ,, ,, ,, + 2 ,, ,, ,, + 1 ,, $Cu(NO_3)_2$,,	0.001	0.0028		∞	0.2	40	2.25	
14	4 ,, ,, ,, + 2 ,, ,, ,, + 1 ,, $CdSO_4$,,	0.001	0.0028	2.25	0.51	0.4	40	2.25	0.0
15	4 ,, ,, ,, + 2 ,, ,, ,, + 1 ,, $Pb(NO_3)_2$,,	0.001	0.0028	2.25	0.49	0.4	40	2.25	0.0
16	4 ,, ,, ,, + 2 ,, ,, ,, + 1 ,, $Th(NO_3)_4$,,	0.001	0.0028	2.25	0.52	0.4	35	2.25	0.0
17	4 ,, ,, ,, + 2 ,, ,, ,, + 1 ,, $TlNO_3$,,	0.001	0.0028	2.25	0.52	0.4	35	2.25	0.0
18	4 ,, ,, ,, + 2 ,, ,, ,, + 1 ,, $Co(NO_3)_2$,,	0.001	0.0028	2.30	0.50	0.4	30	2.25	+2.2
19	4 ,, ,, ,, + 2 ,, ,, ,, + 1 ,, $Ni(NO_3)_2$,,	0.001	0.0028	2.30	0.51	0.4	30	2.25	+2.2
20	4 ,, ,, ,, + 2 ,, ,, ,, + 1 ,, $MnCl_2$,,	0.001	0.0028	2.30	0.54	0.4	30	2.25	+2.2
21	4 ,, ,, ,, + 2 ,, ,, ,, + 1 ,, $Zn(NO_3)_2$,,	0.001	0.0028	2.30	0.57	0.2	40	2.25	+2.2
22	4 ,, ,, ,, + 2 ,, ,, ,, + 1 ,, $Fe(NO_3)_3$,,	0.001	0.0028	2.25	0.57	0.4	45	2.25	0.0
23	4 ,, ,, ,, + 2 ,, ,, ,, + 1 ,, $Ba(NO_3)_2$,,	0.001	0.0028	2.25	0.52	0.2	35	2.25	0.0
24	4 ,, ,, ,, + 2 ,, ,, ,, + 1 ,, $Ca(NO_3)_2$,,	0.001	0.0028	2.25	0.47	0.2	35	2.25	0.0
25	4 ,, ,, ,, + 2 ,, ,, ,, + 1 ,, $Mg(NO_3)_2$,,	0.001	0.0028	2.30	0.57	0.2	45	2.25	+2.2

Experiments 7 and 8 (Table I) are interesting, since in the former case the initial precipitation occurs at the molar ratio of 1 Hg : 0.7 CBM and in the latter the precipitation began at the ratio 1 Hg : 1.4 CBM. This difference in behaviour is caused by the different pH's at which the titration is made.

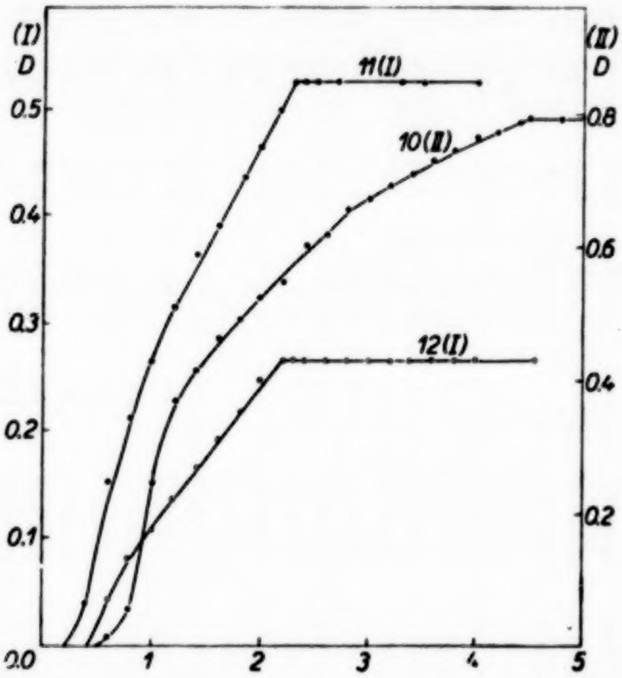

Fig. 2. The precipitation of mercury in the presence of bismuth.

Fig. 2 shows the course of the titrations in the presence of bismuth (molar ratios 1 : 17 to 1 : 66). In these experiments the maximum values obtained were approximately proportional to the amount of mercury analysed (0.3 mg — 1.2 mg Hg).

CONCLUSIONS

On the basis of the experiments presented in this paper, we conclude that *a solution of EDTA containing excesses of ammonia retains all the alien metals* (with the exception of copper) *as complexes* and *that the titration of minute amounts of mercury with NaCBM can be carried out smoothly without any interference.*

The percentage of mercury may be very low, *e.g.* in the case of bismuth, it may be 1% or less.

METHOD

20 ml aqueous solution which contains 0.3-1.2 mg mercuric mercury and any quantity of bivalent metals or polyvalent iron, (aluminium), bismuth or thorium, is analysed directly by heterometric titrations with 0.0028*M* sodium diethyldithiocarbamate.

The solution must contain an excess of ethylendiaminetetraacetate and a corresponding excess of ammonia in order to obtain a high pH. The titration time is 30-40 minutes and the error is 0-2%.

SUMMARY

0.3-1.2 mg mercury in 20 ml aqueous solution is analysed with sodium diethyldithiocarbamate. The solution may contain any amount of other bivalent metal or iron (III), bismuth or thorium. A corresponding excess of ethylenediaminetetraacetate and ammonia must then be added. The error is 0-2%.

RÉSUMÉ

0.3 à 1.2 mg de mercure dans 20 ml de solution aqueuse peuvent être dosés au moyen de diéthyldithiocarbamate de sodium. Ce dosage peut être effectué en présence d'autres cations bivalents et en présence de fer (III), de bismuth et de thorium. Un excès correspondant d'éthylènediaminetétraacétate et d'ammoniaque doit alors être ajouté. L'erreur est comprise entre 0 et 2%.

ZUSAMMENFASSUNG

0.3-1.2 mg Quecksilber in 20 ml wässriger Lösung werden mit Natriumdiäthyldithiocarbamat analysiert. Die Lösung kann beliebige Mengen anderer zweiwertiger Metalle sowie Eisen (III), Wismuth oder Thorium enthalten. Ein entsprechender Überschuss an Äthylendiamintetraacetat und Ammoniak muss dann hinzugefügt werden. Fehler: 0-2%.

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THE AURINTRICARBOXYLATES OF ALUMINIUM, IRON AND CHROMIUM

COMPOSITION, STRUCTURE AND ANALYTICAL USE
A HETEROMETRIC STUDY

by

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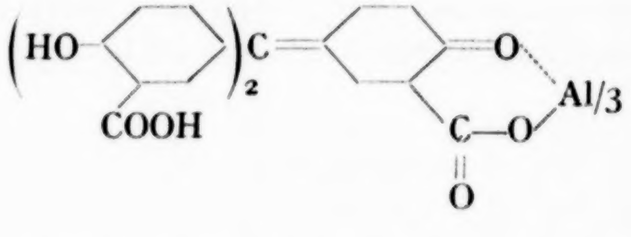
INTRODUCTION

Ammonium aurintricarboxylate (aluminon = AN) is used extensively for the detection of aluminium and for the quantitative determination of aluminium, beryllium *etc.*[1] The composition of the compounds which are obtained at different pH's have not been thoroughly investigated. In the case of aluminium, the compound obtained from slightly acid solution is generally presented as:



The analytical aspect of the problem is connected with the colour intensity and the stability of the compounds obtained at different pH's. An intense red solution is obtained and the intensity of the colour is measured. The presence of iron or chromium interferes with the results obtained in an analysis of an aluminium solution. The hypothesis generally accepted is that the AN forms "lakes" with the cations. The study of the character and the composition of the „lakes" involves great difficulties as no methods exist for their study. As the study of chemical reactions in suspensions is of special concern to us, we were interested in investigating the reactions with AN and in seeing to what extent they proceed stoichiometrically, and if and when precipitation occurs.

Our study was limited to the trivalent cations. Preliminary heterometric titrations with other bi- and polyvalent cations were carried out in order to obtain a general picture of the reaction of cations with AN. From our experiments it could be deduced that all the trivalent cations form a series of well defined compounds with AN. These were formed successively from one another on the addition of AN to the cation or vice versa. The existence of both intermediates and final compounds was established. The heterometric titrations were completed in a short time and the reactions studied proceeded smoothly and stoichiometrically.

The compounds of iron were much more stable than those of aluminium or chromium. Even in a solution with a molar ratio of 100 Al : 1 Fe the iron compounds were formed first and quantitatively.

The analytical aspect of the investigation was studied separately.

EXPERIMENTAL

The same apparatus and the same working conditions were observed as in previous heterometric investigations[2-3]. The temperature of the reaction vessel was thermostatically controlled during the titration. All titrations were carried out at 20° C. The reaction vessel had a diameter of 4 cm.

The reagents used were all c.p. or analytical reagents. No difference in the results was observed whether the trivalent salts were chlorides or nitrates. In order to avoid hydrolysis, all dilute solutions of iron were prepared from an iron nitrate stock solution ($0.1M$) which contained added free nitric acid in a molar concentration twice as high as the molarity of the iron nitrate (*e.g.* a $0.005M$ $Fe(NO_3)_3$ solution was $0.01M$ in HNO_3). The highly diluted solutions of iron nitrate were nevertheless freshly prepared from the more concentrated stock solutions. The AN used was a BDH c.p. reagent.

The isolation of the solid compounds

A deep red Corning filter (No. 2408) was used throughout this investigation. This was done in order to eliminate, as far as possible, the colour effect of AN during the titration and to measure the density caused by the formation of the precipitation only. It cannot be said with certainty to what extent this goal was achieved as we were working in a complicated sol-gel system. The clear breaks at the critical end-points in the curves presented prove that the guiding principles held in all cases, and the breaks obtained corresponded to the quantitative formation of solid compounds of definite composition.

Reaction time

Generally in the more important titrations the time necessary for a full titration was between ten and twenty minutes. But in special cases when additional information was of interest, the titration time was extended somewhat. This indicates that the reactions studied are of a relatively simple nature. No complications whatsoever were caused by the physical state of the precipitates as compared with other precipitates which have been studied heterometrically.

RESULTS AND DISCUSSION

A. The reaction between aluminium and AN

pH-Heterometric titrations

Fig. 1 presents the composition and results of heterometric titrations which were carried out by the dropwise addition of nitric acid to solutions containing a buffer mixture in addition to aluminium and AN. Curve 4 shows a parallel blank pH-titration carried out with the buffer mixture. The pH's of expts. 1-3 can be taken from this curve. The heterometric titrations were carried out in solutions of a molar ratio 1 Al : 1 AN (curve 1), 1 Al : 2 AN (curve 2) and 1 Al : 3 AN (curve 3). No other molar ratios were ever found at the critical points of the heterometric titrations. Analysing the curves of Fig. 1. the following may be deduced: no precipitation occurred at high pH's in any experiment. In expt. 1. (1 Al : 1 AN) the precipitation practically began at pH $\sim$ 8 and was completed at pH $\sim$ 4. The precipitate was of bright red color. At lower pH's the precipitate very slowly dissolved. The results of expts. 2 (1 Al : 2 AN) and 3 (1 Al : 3 AN) are more definite and clearer. In both cases the precipitation began at pH $\sim$ 6 and was completed at pH $\sim$ 3. Whilst in expt. 2 some decrease in the densities occurred at pH < 2, no influence whatever was noticeable in expt. 3. The character of the lower parts of curves 2 and especially 3, indicates that in the pH region of 4-6 the course of the precipitation is somewhat different than in the pH region of 3-4. Summarizing, it may be said that aluminium may be precipitated either as $Al(AN)_2$ or $Al(AN)_3$ at pH's ~ 3- ~ 4.

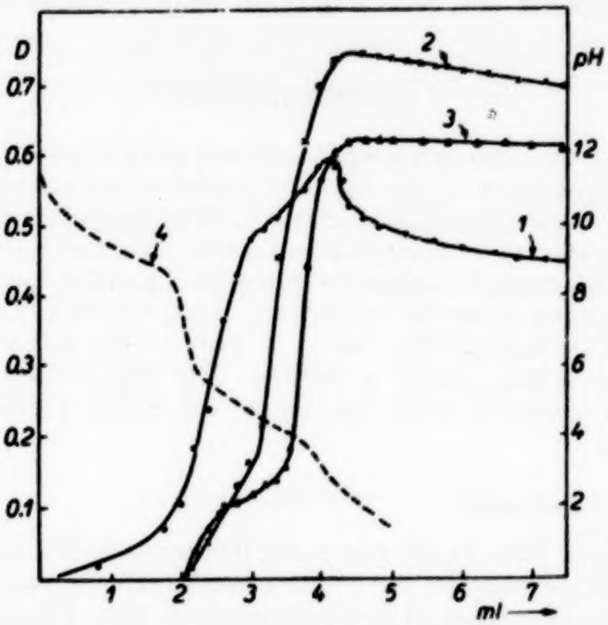


Fig. 1

1. 3 ml $0.02M$ $AlCl_3$ + 3 ml $0.02M$ Aluminon + 2 ml M CH_3COOH + 2 ml M NH_4NO_3 + 4.5 ml M NaOH + 5.5 ml H_2O + x ml M HNO_3.
2. 2 ml $0.02M$ $AlCl_3$ + 4 ml $0.02M$ Aluminon + 2 ml M CH_3COOH + 2 ml M NH_4NO_3 + 4.5 ml M NaOH + 5.5 ml H_2O + x ml M HNO_3.
3. 2 ml $0.02M$ $AlCl_3$ + 6 ml $0.02M$ Aluminon + 2 ml M CH_3COOH + 2 ml M NH_4NO_3 + 4.5 ml M NaOH + 3.4 ml H_2O + x ml M HNO_3.
4. pH curve blank. Titration time, 15-30 minutes.

Titrations of aluminium with AN

Fig. 2 presents a selection of results obtained with $AlCl_3$ or $Al(NO_3)_3$ in the presence or in the absence of excesses of acetic acid. In all cases the *first* maximum optical density point was obtained exactly at the calculated point of the quantitative formation of $Al(AN)_3\downarrow\downarrow$. No other intermediates were obtained. The values of the maximum density in curves 1 and 2 were almost proportional to the concentration of aluminium. In acetic acid solutions (curves 3 and 4) lower values were obtained.

Titrations of AN with aluminium

Fig. 3 presents the composition and the results of some experiments. When AN was titrated with Al, the first maximum optical density was obtained, in all curves, exactly at the calculated point on the abscissa for the quantitative formation of $Al(AN)_2\downarrow\downarrow$. On further addition of aluminium, a horizontal density line was obtained, indicating that the compound is final. In curves 2 and 4, the existence of a more soluble compound of the composition $Al(AN)_3$ could be traced, but this compound was then transformed into $Al(AN)_2\downarrow\downarrow$. In these titrations no proportionality seemed to exist between the values of the maximum density and the amount of AN which was titrated.

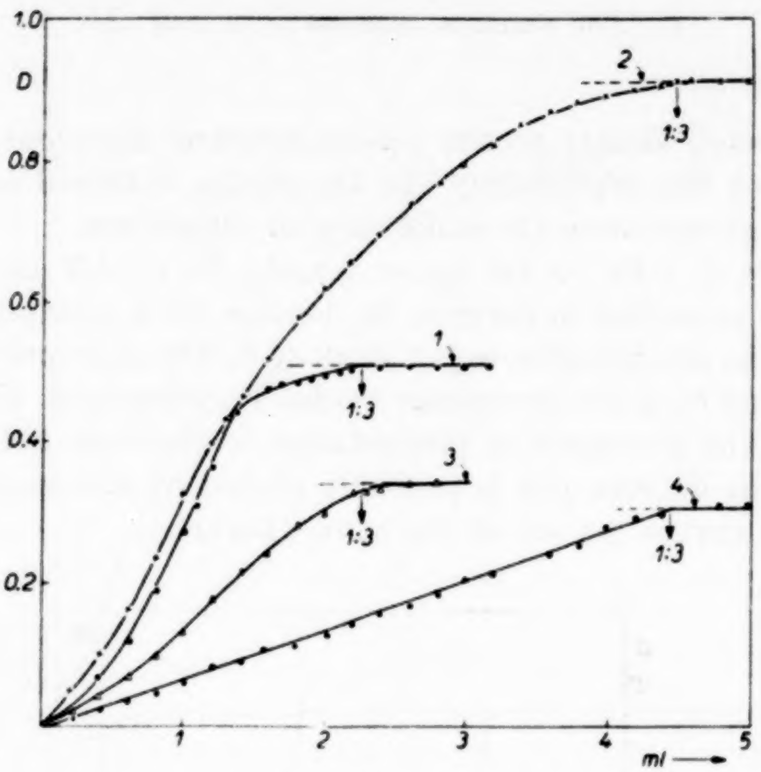


Fig. 2

1. 3 ml 0.005M $AlCl_3$ + 7 ml H_2O + x ml 0.02M Aluminon.
2. 3 ml 0.01M $AlCl_3$ + 7 ml H_2O + x ml 0.02M Aluminon.
3. 3 ml 0.005M $Al(NO_3)_3$ + 1 ml M CH_3COOH + 6 ml H_2O + x ml 0.02M Aluminon.
4. 3 ml 0.005M $Al(NO_3)_3$ + 1 ml M CH_3COOH + 6 ml H_2O + x ml 0.01M Aluminon.

Titration time, 20 minutes. Red filter.

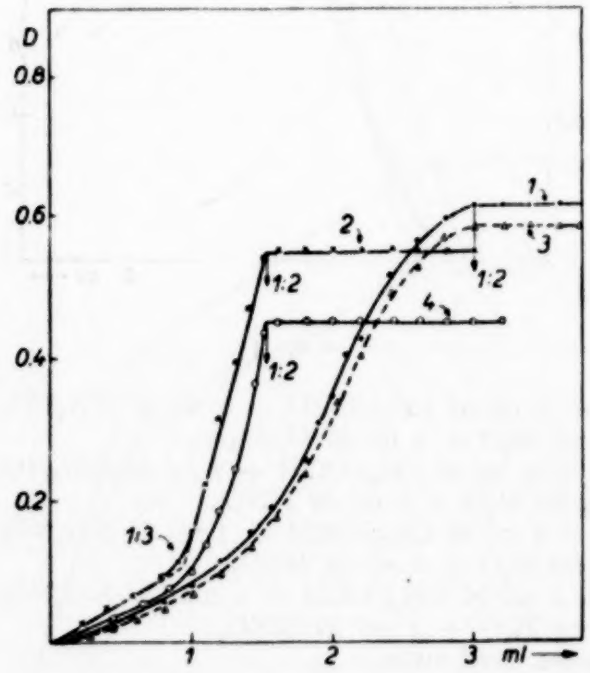


Fig. 3

1. 3 ml 0.02M Aluminon + 7 ml H_2O + x ml 0.01M $AlCl_3$.
2. 3 ml 0.01M Aluminon + 7 ml H_2O + x ml 0.01M $AlCl_3$.
3. 3 ml 0.02M Aluminon + 1 ml M CH_3COOH + 6 ml H_2O + x ml 0.01M $Al(NO_3)_3$.
4. 3 ml 0.01M Aluminon + 1 ml M CH_3COOH + 6 ml H_2O + x ml 0.01M $Al(NO_3)_3$.

Titration time, 20 minutes. Red filter.

B. The reaction between iron and AN

pH-Heterometric titrations

The titrations were similar to the pH-heterometric titrations with aluminium. The composition of the experiments and the results obtained are seen in Fig. 4. The molar ratios chosen were the same as with aluminium:
1 Fe : 1 AN (curve 5), 1 Fe : 2 AN (curve 4) and 1 Fe : 3 AN (curves 2 and 3). The blank pH curve is presented in curve 1. In no case did a precipitation occur at pH > 9. In all cases the precipitation began at pH ∿ 8. The main precipitation occurred at pH 6-4. Below pH ∿ 4 the precipitate gradually redissolved. The precipitate was of violet colour. The pH-region of precipitation is therefore between 8 and 4. In the case of iron the decisive role is probably played by the compound $Fe^{III}{}_1(AN)_1$ and therefore the curves 3-5 are of the same character.

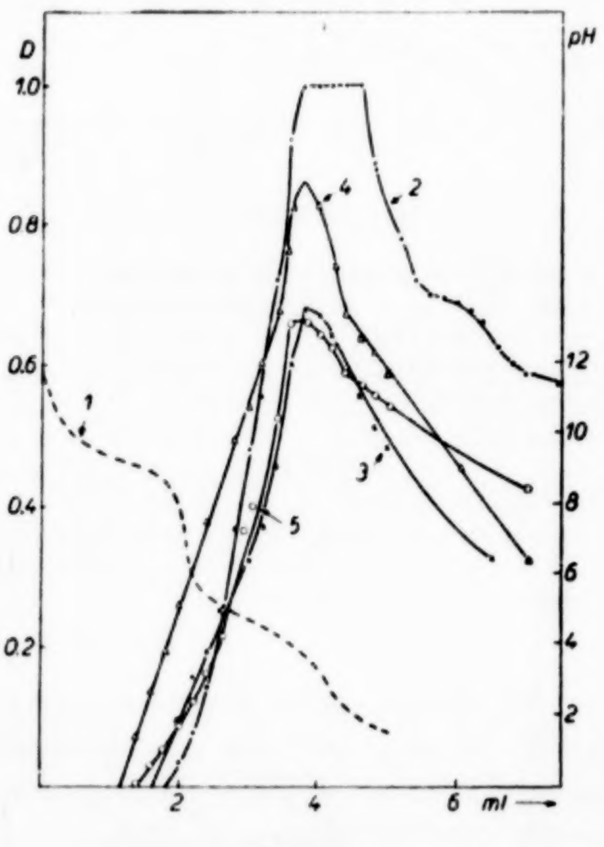


Fig. 4

1. pH blank curve.
2. 2 ml 0.005M $Fe(NO_3)_3$ + 2 ml M CH_3COOH + 2 ml M NH_4NO_3 + 4 ml M NaOH + 6 ml 0.005M Aluminon + 4 ml H_2O + x ml M HNO_3.
3. 2 ml 0.0025M $Fe(NO_3)_3$ + 2 ml M CH_3COOH + 2 ml M NH_4NO_3 + 4 ml M NaOH + 6 ml 0.0025M Aluminon + 4 ml H_2O + x ml M HNO_3.
4. 2 ml 0.005M $Fe(NO_3)_3$ + 2 ml M CH_3COOH + 2 ml M NH_4NO_3 + 4 ml M NaOH + 4 ml 0.005M Aluminon + 6 ml H_2O + x ml M HNO_3.
5. 2 ml 0.01M $Fe(NO_3)_3$ + 2 ml M CH_3COOH + 2 mal M NH_4NO_3 + 4 ml M NaOH + 2 ml 0.01M Aluminon + 8 ml H_2O + x ml M HNO_3.
Titration time, 10 minutes. Red filter.

Titrations of iron with AN

Fig. 5 presents the composition and results of titrations carried out in the absence of acetic acid. The same amount of iron was titrated with AN of different concentrations. Fig. 6 shows similar titrations but in the presence of excesses of acetic

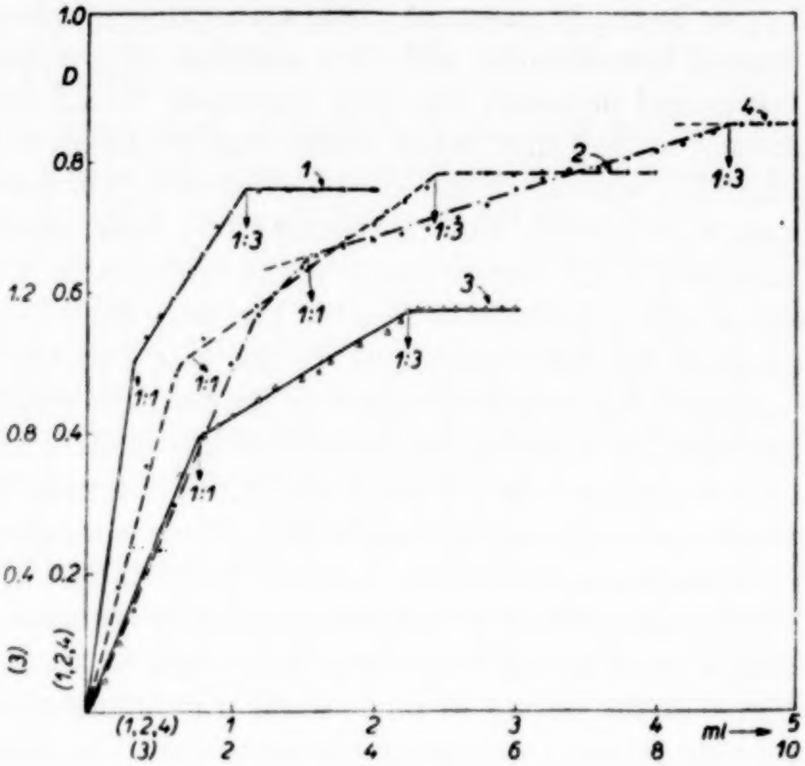


Fig. 5

1. 3 ml $0.0025M$ $Fe(NO_3)_3$ + 7 ml H_2O + x ml $0.02M$ Aluminon.
2. 3 ml $0.0025M$ $Fe(NO_3)_3$ + 7 ml H_2O + x ml $0.01M$ Aluminon.
3. 3 ml $0.0025M$ $Fe(NO_3)_3$ + 7 ml H_2O + x ml $0.005M$ Aluminon.
Titration time, 20 minutes. Red filter.

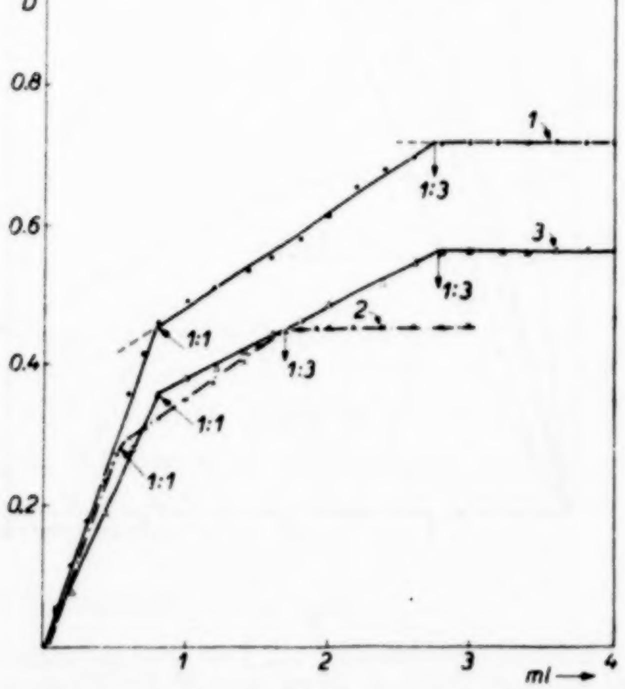


Fig. 6

1. 5 ml $0.00125M$ $Fe(NO_3)_3$ + 1 ml M CH_3COOH + 4 ml H_2O + x ml $0.0066M$ Aluminon.
2. 3 ml $0.00125M$ $Fe(NO_3)_3$ + 1 ml M CH_3COOH + 6 ml H_2O + x ml $0.0066M$ Aluminon.
3. 5 ml $0.00125M$ $Fe(NO_3)_3$ + 1 ml $0.1M$ HNO_3 + 4 ml H_2O + x ml $0.0066M$ Aluminon.
Titration time, 10-15 minutes. Red filter.

acid (curves 1 and 2) or in the presence of nitric acid (curve 3). In all cases in Fig. 5 precipitation occurred immediately with the addition of the first drop of AN, showing that the compound obtained was very insoluble. In all cases the densities rose steeply and linearly to the first break which was obtained at the molar ratio of 1 Fe : 1 AN. $Fe_1(AN)_1$ was precipitated quantitatively. On further addition of AN the density again rose linearly but the density line took another direction. A second break was obtained in all cases exactly at the molar ratio of 1 Fe : 3 AN↓↓. On further addition of AN a horizontal density line was then obtained. Excesses of AN had no influence on the final compound. In this case also, the titrations lasted 10-20 minutes. The course of the titration, as well as the densities which were obtained, did not change noticeably on varying the concentration of AN. The above breaks in each curve can also be utilized for an exact and rapid determination of iron(III).

As far as the influence of acids on the results (Fig. 6) are concerned, the following may be said: with the same amount of iron used for the titration, the density values at the breaks are of the same order of magnitude with or without acetic acid. The density values obtained (curves 1 and 2) are proportional to the amount of iron in solution. The character of the curves of Figs. 5 and 6 indicates that the precipitate is very regular, probably giving particles of the same size. The presence of excesses of a strong acid (HNO_3) seems to depress the density values obtained (curve 3).

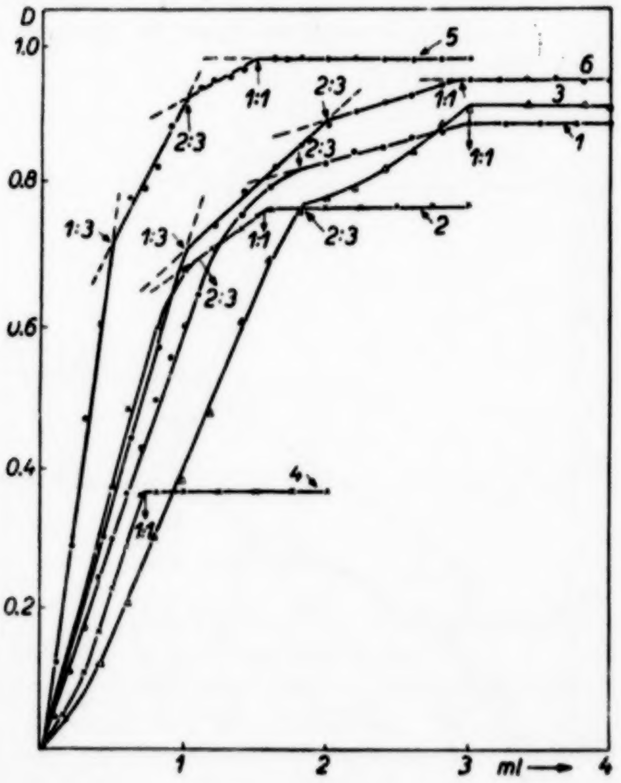


Fig. 7

1. 3 ml 0.01M Aluminon + 7 ml H_2O + x ml 0.01M $Fe(NO_3)_3$
2. 3 ml 0.005M Aluminon + 7 ml H_2O + x ml 0.01M $Fe(NO_3)_3$
3. 3 ml 0.005M Aluminon + 7 ml H_2O + x ml 0.01M $Fe(NO_3)_3$
4. 2 ml 0.002M Aluminon + 8 ml H_2O + x ml 0.005M $Fe(NO_3)_3$
5. 3 ml 0.005M Aluminon + 1 ml 0.1M CH_3COOH + 6 ml H_2O + x ml 0.01M $Fe(NO_3)_3$
6. 3 ml 0.005M Aluminon + 1 ml 0.1M CH_3COOH + 6 ml H_2O + x ml 0.005M $Fe(NO_3)_3$

Titration time, 10 minutes. Red filter.

C. Reaction between chromium(III) and AN

pH-Heterometric titrations

Buffer mixtures, were used, similar to those used in the case of aluminium (or iron), but as the chromium was less sensitive to AN than the other metals, the mixtures contained higher concentrations of AN (*cf.* Fig. 8).

In the presence of a buffer mixture identical to that used previously, a brown precipitate was obtained even before the addition of nitric acid. An acid buffer mixture was therefore tried instead (composition: 2 ml NH_4NO_3 *M* + 2 ml CH_3COOH *M* + 1 ml HNO_3 *M*) with the intention of titrating with NaOH, but unfortunately a red precipitate appeared even before the addition of the base. We were therefore compelled to give up the idea of such titrations.

Titrations of chromium with AN

Fig. 8 shows the composition and results of titrations of chromium with AN. Only curve 1 shows breaks at 1 Cr : 1 AN and possibly 1 Cr : 2 AN. On titrating with a more highly concentrated AN-solution, no clear breaks were obtained.

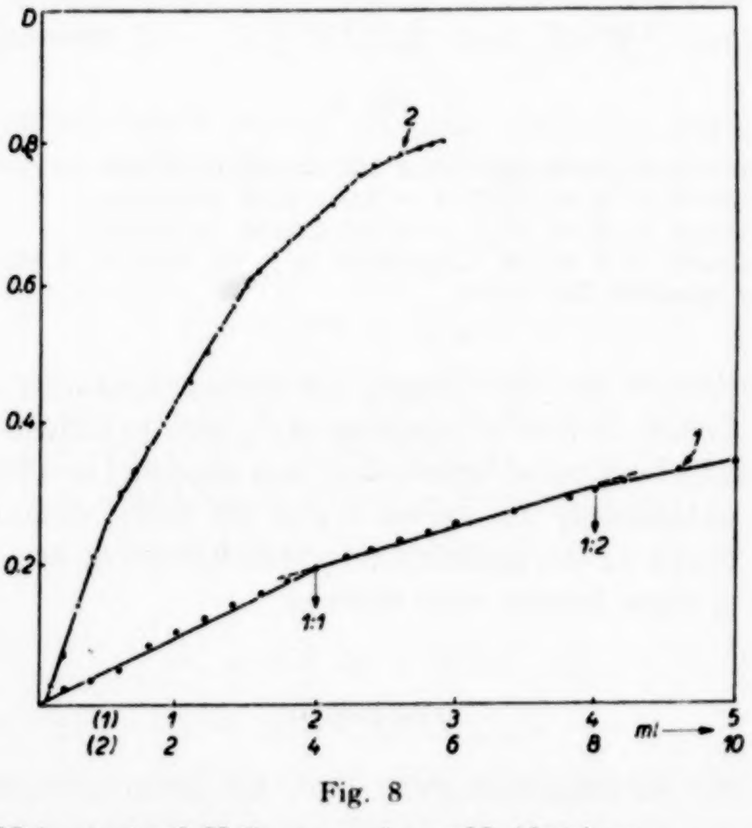


Fig. 8

1. 4 ml 0.005*M* $Cr(NO_3)_3$ + 6 ml H_2O + *x* ml 0.01*M* Aluminon.
2. 4 ml 0.01*M* $Cr(NO_3)_3$ + 6 ml H_2O + *x* ml 0.02*M* Aluminon.
Titration time, 15 minutes. Red filter.

Titrations of AN with chromium

In contrast to the results shown in Fig. 8 clear breaks were obtained in the reverse titrations of AN with $Cr(NO_3)_3$ (Fig. 9). Curves 1-3 show results of titrations carried out in the absence of acetic acid. Curve 4 gives the results of a titration of identical composition to that of curve 3, but containing, in addition, acetic acid. The sensitivity of the chromium towards acetic acid is surprising: the densities obtained in the presence of acetic acid are almost one third as high as those obtained in its absence.

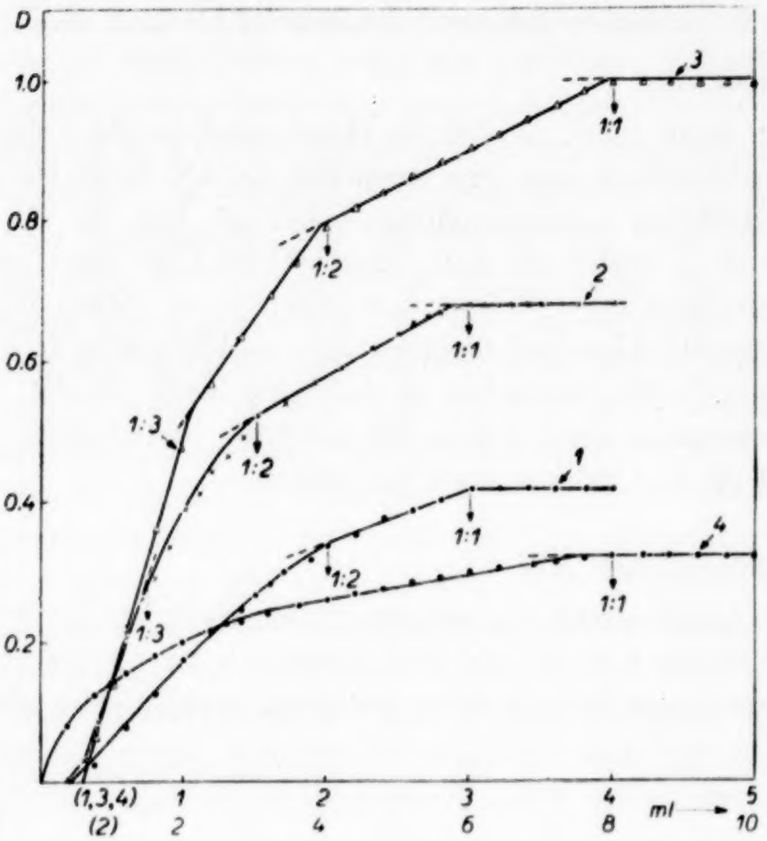


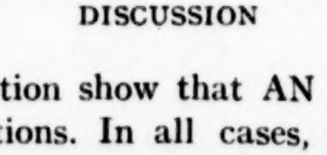
Fig. 9

1. 3 ml 0.01M Aluminon + 7 ml H_2O + x ml 0.01M $Cr(NO_3)_3$.
2. 6 ml 0.01M Aluminon + 4 ml H_2O + x ml 0.01M $Cr(NO_3)_3$.
3. 4 ml 0.02M Aluminon + 6 ml H_2O + x ml 0.02M $Cr(NO_3)_3$.
4. 4 ml 0.02M Aluminon + 1 ml M CH_3COOH + 5 ml H_2O + x ml 0.02M $Cr(NO_3)_3$.
Titration time, 20 minutes. Red filter.

In all four experiments the final break was obtained exactly at the molar ratio of 1 Cr : 1 AN (= CrAN). A further addition of Cr had no influence whatever on the compound CrAN and a horizontal density line was obtained in all cases. Intermediate clear breaks were obtained in the curves 1-3 at the molar ratio of 1 Cr : 2 AN (= $Cr(AN)_2$). A clear break at the ratio 1 Cr : 3 AN ($Cr(AN)_3$) was detectable only in curve 3. In curve 4 these breaks were blurred.

DISCUSSION

The results of this investigation show that AN gives precipitates of a definite composition with all three cations. In all cases, stoichiometric reactions occur. The optimum pH at which these precipitations occur is pH ∿ 4. In the case of iron, precipitation occurs at pH 7-8 and with chromium the precipitate is formed at even higher pH's. In contrast to these, aluminium forms detectable precipitates with AN only in acid solutions at pH 4-6. It is difficult to describe with certainty the character of the compounds which are formed in alkaline solutions. They may be neutralized oxycomplexes which are formed in solution and which have the group:



Thus, during the study of the pH condition of the formation of the precipitates, a picture was obtained of the pH conditions which were necessary to hold the compounds "dissolved".

From the working conditions at 20° C it could be seen that 10-20 minutes were sufficient to obtain a detailed heterometric curve with all its breaks (= critical points). It can therefore be concluded that both the intermediate and the final reactions proceed smoothly and are not affected by the physical nature of the precipitates. It is remarkable how easily an intermediate *insoluble* compound is transformed quantitatively on the addition of either AN or Me^{+3}, into another insoluble compound.

With regard to the composition of the final insoluble compounds which were obtained on the addition of Me^{+3} to AN, in the case of iron or chromium they were composed as $Me^{III}_1\,(AN)_1 \downarrow\downarrow$ whilst in the case of aluminium $Al(AN)_2$ was obtained. It is surprising that $Al_1\,(AN)_1$ does not exist as an insoluble compound. On the other hand, in the case of iron an insoluble compound $Fe(AN)_2$ was never detected. In the case of chromium only the titrations in which Cr was added to AN gave clear-cut results: insoluble compounds of the composition $Cr(AN)_2 \downarrow$ and $Cr_1(AN)_1 \downarrow\downarrow$ were formed. $Cr(AN)_3$ could only be detected in certain experiments.

The composition of the insoluble compounds obtained with chromium were partly analogous to aluminium (= $Me^{III}(AN)_2$) and partly analogous to iron (= $Me^{III}_1(AN)_1$).

The different reactions which are of an ionic character are presented below, without consideration of the charges of the ionic components.

I. a Me^{+3} + *x AN*:

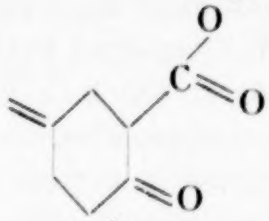
1. $Al + 3\,AN \rightarrow Al(AN)_3 \downarrow\downarrow$
2. $Fe + AN \rightarrow Fe_1(AN)_1 \downarrow$
3. $Fe_1(AN)_1 + 2\,AN \rightarrow Fe(AN)_3 \downarrow\downarrow$
4. $(Cr + AN \rightarrow Cr_1\,(AN)_1 \downarrow)$

II. a AN + *x* Me^{+3}:

5. $(3\,AN + Al \rightarrow Al(AN)_3 \downarrow)$
6. $(2\,Al(AN)_3 + Al \rightarrow 3\,Al(AN)_2 \downarrow\downarrow)$
7. $2\,AN + Al \rightarrow Al(AN)_2 \downarrow\downarrow$
8. $(3\,AN + Fe \rightarrow Fe(AN)_3 \downarrow ?)$
9. $(Fe(AN)_3 + Fe \rightarrow Fe_2(AN)_3 \downarrow)$
10. $3\,AN + 2\,Fe \rightarrow Fe_2(AN)_3 \downarrow$
11. $Fe_2(AN)_3 + Fe \rightarrow 3\,Fe_1(AN)_1 \downarrow\downarrow$
12. $3\,AN + Cr \rightarrow Cr(AN)_3 \downarrow$
13. $2\,Cr(AN)_3 + Cr \rightarrow 3\,Cr(AN)_2 \downarrow$
14. $2\,AN + Cr \rightarrow Cr(AN)_2 \downarrow$
15. $Cr(AN)_2 + Cr \rightarrow 2\,Cr_1(AN)_1 \downarrow\downarrow$

(The compounds underlined are those corresponding to the clear breaks in heterometric curves.) Of the different compounds obtained those of iron are probably the most stable. When the mixtures, which contain traces of iron, and both chromium and aluminium in large excesses, were titrated with AN, the reaction proceeded quantitatively with iron alone at first.

The remarkable fact must be established that in our investigation on AN we never met with compounds which contained *more* than *one* mol cation per *one* mol AN. We may see the reason for this in the electronic structure of the chinoide formula which prevents the other salicylate-groups from functioning freely. It must therefore be assumed that of the *three* pairs of carboxylic and hydroxy-groups merely *one* pair can function in the complex formation. This group is probably as follows:



SUMMARY

1. With all three cations, insoluble, well-defined compounds were obtained. These are formed successively one from another.
2. The reactions proceeded smoothly and stoichiometrically, giving compounds of the molar ratios of cation to aluminon: 1:1, 1:2, and 1:3.
3. The pH-heterometric conditions of the precipitation were studied in each case.
4. Formulas for the single reactions are given in the paper.
5. The analytical aspect of the determination of traces of iron in the presence of excesses of aluminium and chromium, was emphasized in the investigation.

RÉSUMÉ

1. Des composés insolubles et bien définis ont été obtenus avec les trois cations étudiés. Ils se forment successivement, l'un provenant de l'autre.
2. Les réactions s'effectuent régulièrement et stoechiométriquement, dans les rapports moléculaires cation/aluminon suivants: 1:1, 1:2 et 1:3.
3. Les conditions de pH de précipitation ont été étudiées dans chaque cas.
4. Les équations des réactions sont données.
5. Le côté analytique du dosage des traces de fer, en présence d'excès d'aluminium et de chrome, a été particulièrement développé.

ZUSAMMENFASSUNG

1. Genau definierte Verbindungen wurden mit allen drei Kationen erhalten. Diese Verbindungen enstehen sukzessive aus einander.
2. Die Reaktionen verlaufen glatt und stöchiometrisch. Verbindungen von molarem Verhältnis von Kation zu Aluminon gleich 1:1, 1:2 und 1:3 wurden erhalten.
3. Die pH-heterometrischen Bedingungen der Fällung wurden in jedem einzelnen Fall studiert.
4. Die Formulierung der einzelnen Reaktionen wird in der Arbeit dargestellt.
5. Die Möglichkeit der Spurenbestimmung von Eisen in Aluminium und Chrom wird betont.

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MEASUREMENTS IN THE ULTRAVIOLET REGION OF APPARENT ABSORPTION BY BARIUM SULFATE SOLS

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The exact relationship between the absorbance of a suspension and the wavelength of incident light depends upon several parameters, and, indeed, extensive theoretical and experimental work has made possible the use of absorption measurements as a method for the estimation of particle size[1,2,3]. In general, "Tyndall spectra" show an increase in the apparent absorption with a decrease in the wavelength of the source. Recent work by FOG[4] has shown that one can apply corrections for the presence of turbidity in order to determine the amount of true absorption. He employed a plot of the logarithm of the absorptivity against the logarithm of the wavelength, a plot which HELLER AND VASSY[5] had pointed out earlier could be used as a means of distinguishing between true and apparent absorption.

This plot results in an approximately straight line over a range of 100 mμ, and has a slope which is dependent upon the average particle size of the suspension. The smaller particles result in steeper slopes. HELLER, KLEVENS AND OPPENHEIMER[6] established a calibration curve relating particle size to the slope of the log plot for the cases where the refractive index ratio was 1.24 ± 0.01.

In the present study, absorbance measurements were made in the ultraviolet region in order to take advantage of the increase in scattering at shorter wavelengths as a means of extending the technique to the dilute sols produced for nephelometric measurement. Thus, it was hoped that the technique would provide qualitative information about changes in the average particle size of the barium sulfate sols which in turn would be useful in describing the effects of different variables on the nephelometric sensitivity and the stability of the suspensions. These variables include the method of precipitation, the effect of high concentrations of foreign salts, and changes in ethanol content of the solutions. Because nothing was known about the form of the distribution of particle sizes in the polydispersed sols of barium sulfate, no attempt was made to calculate average particle size. It was realized that other techniques, such as angular-dependence light scattering would be required to provide information about the particle-size distribution[7].

Another objective of this investigation was to compare the relative sensitivities of absorption measurements in the ultraviolet with nephelometric measurements of 90°-scattered light.

EXPERIMENTAL DETAILS

Apparatus

All spectra were taken on a Cary, Model 11, recording spectrophotometer which was used to record the wavelength region from 350 to 220 mμ in approximately 1 minute. The wavelength was always scanned in the same direction. The 100% transmission line was established with a blank which contained all of the components of the final solutions except sulfate. Matched 10-cm cell were employed.

Data relating the concentration of sulfate to the absorbance were obtained using a Beckman DU spectrophotometer and the same 10-cm cells. These absorbance measurements, including those of the blanks, were taken with reference to distilled water. An appropriate cell correction of the order of 0.007 absorbance unit was applied.

A Model 7 Coleman photonephelometer, equipped with the usual cuvettes, was used for the nephelometric analysis of the calcium chloride solutions. The sensitivity of the instrument was established in terms of Coleman nephelos standards.

Measurements of pH were made with a glass electrode in conjunction with a Beckman Model G pH meter. A Fisher refractometer was employed to determine approximate values of refractive indices of solutions.

Preparation of solutions

Calcium chloride solutions were prepared from the "low alkali" calcium carbonate sold by Mallinckrodt Chemical Works. This reagent-grade chemical was analysed nephelometrically, and, as previously reported[8], was found to be essentially sulfate-free. Two hundred grams of the calcium carbonate, weighed on a trip balance, were slurried with approximately 500 ml of distilled water. Three hundred and thirty ml of concentrated (37%) hydrochloric acid were added very slowly using both a pipet (100 ml) and a buret to deliver the acid. After the solution had been boiled to expel carbon dioxide, it was cooled to room temperature. Its pH was 2.0 .

The solution was filtered through S and S black ribbon filter paper, and distilled water was added to bring the volume to approximately 980 ml. The pH was then adjusted to 1.0 by the addition of a few milliliters of 1:10 hydrochloric acid solution. Finally, the solution was transferred to a 1-liter volumetric flask and brought to exact volume with a pH 1.00 solution of hydrochloric acid. The final solution was 2.00*M* in calcium chloride (0.200 g $CaCO_3$ per ml), and had a pH of 0.98.

As previously reported[8], the acidity of this solution cannot be defined accurately in terms of concentration because of its high ionic strength. It was thought advisable to define its acidity in terms of $\triangle$ $pH_{1/2}$ values that have been applied to buffers[9]. To do this, 25.00 ml of the 2.00*M* calcium chloride solution were diluted to 50.00 ml with distilled water. The change in pH was 0.77 unit instead of 0.30. An analogous experiment, performed by diluting 25.00 ml of the calcium solution to 50.00 ml with a hydrochloric acid solution of pH 1.00, resulted in a $\triangle$ $pH_{1/2}$ of -0.17 rather than showing no change. Thus the observed pH value is not a simple function of the concentration of the acid in such systems.

From the 2.00*M* solution of calcium chloride, two solutions were prepared, each of which was 1.00*M* in calcium chloride and 20% by volume of ethanol. Before these solutions were brought to final volume with a pH 1.0 hydrochloric acid solution, enough sulfate was added to one of them, in the form of a standard solution of potassium sulfate (containing 125 μg per ml of sulfate and enough hydrochloric acid to give it a pH of 1.0), to produce a solution with a final sulfate concentration of 10.0 μg per ml. No sulfate was added to the other solution, but, because of the sulfate impurity in the hydrochloric acid used to dissolve the calcium carbonate, sulfate was present though the amount was estimated to be less than 0.2 μg per ml. The light scattered by the resulting barium sulfate could be ignored. Concentrations of sulfate between zero and 10 μg per ml were used to obtain calibration curves in 1.0*M* calcium chloride and were prepared by mixing the required amounts of these two solutions.

Three solutions were prepared from a standard solution of potassium sulfate (250 μg per ml) to contain 0, 10.0 and 20.0 μg per ml of sulfate. Each solution was 0.1*M* in hydrochloric acid and 20% by volume ethanol. Six solutions, each containing 10.0 μg per ml of sulfate and 0.1*M* hydrochloric acid were made at 0%, 10%, 30%, 40%, 50% and 60% by volume of ethanol.

A solution of barium chloride was prepared to be 20% by volume of ethanol, 0.1*M* in hydrochloric acid and 0.178*M* in barium chloride.

The alcohol used in the preparation of all of the above solutions was U.S.P. absolute ethanol which was obtained from U.S. Industrial Chemicals Company in pint bottles. When ethanol from larger containers (5 gal) was used, a residual turbidity was found to develop, even in the absence of barium chloride, whenever the ethanol was diluted to 20% by volume with 0.1*M* hydrochloric acid alone.

Precipitation procedure

The same precipitation procedure was used as in the previous nephelometric study[8], *i.e.*, solid barium chloride dihydrate crystals (30-40 mesh) were added to a 40.00 ml portion of solution using a small scoop and were dissolved by motor-stirring for a three-minute period. The final concentration of barium chloride was 0.089M.

One precipitation experiment was run using the technique of mixing equal volumes of a barium chloride solution and a sulfate solution as recommended by TOENNIES AND BAKAY[10]. A 20.00 ml portion of 0.178M barium chloride solution was added to 20.00 ml of the 20.00 µg per ml solution of sulfate to produce a final mixture equivalent to those produced with the solid reagent.

Filtration of the solutions prior to precipitation of the barium sulfate was omitted because the Millipore filters previously used[8] were found to contaminate the solutions with a substance that absorbed below 290 mµ. Fortunately, filtration had been found not to be critical when the concentration of sulfate was greater than 2.0 µg per ml.

RESULTS

Spectral data

Typical curves from the Cary spectrophotometer, obtained for barium sulfate sols produced by 10.0 µg per ml of sulfate, are shown in Fig. 1. The changes in the spectra with time were followed by making successive recordings at convenient intervals of time without disturbing the cells. The time was measured from the moment of addition of the reagent, and therefore included the time required to dissolve the solid barium chloride.

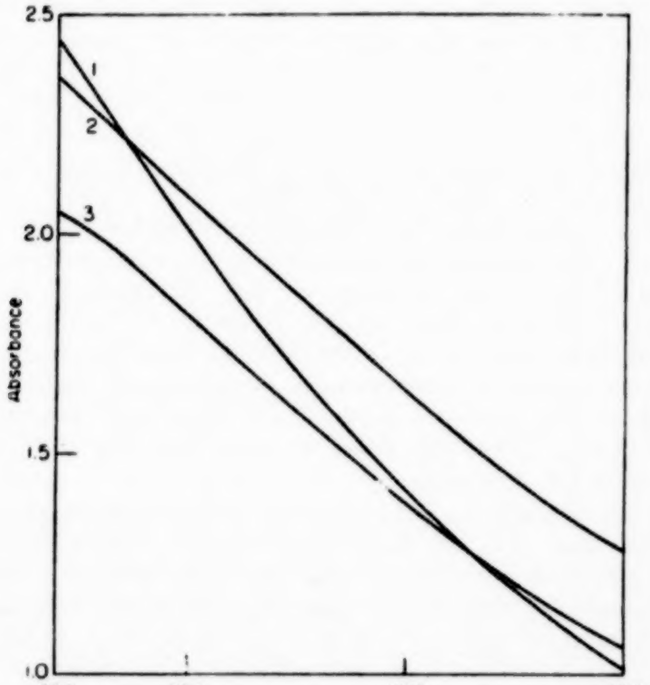

Fig. 1. Spectra of sols produced by 10.0 µg per ml of sulfate.
Curve 1. 20% ethanol after 6 min
Curve 2. 20% ethanol after 74 min
Curve 3. 1.00M $CaCl_2$, 20% ethanol after 7 min

The effect of the ethanol content at two levels, 10% and 20% by volume, on the spectra produced by sols resulting from a concentration of 10.0 µg per ml of sulfate is shown in Fig. 2 and, in addition, the results for a sol containing no ethanol. This figure summarizes the spectra by showing the absorbances at 230 mµ, 280 mµ, and 330 mµ as a function of time. At 230 mµ, only a slight increase in absorbance was observed after the first five minutes, and with time the absorbances decreased

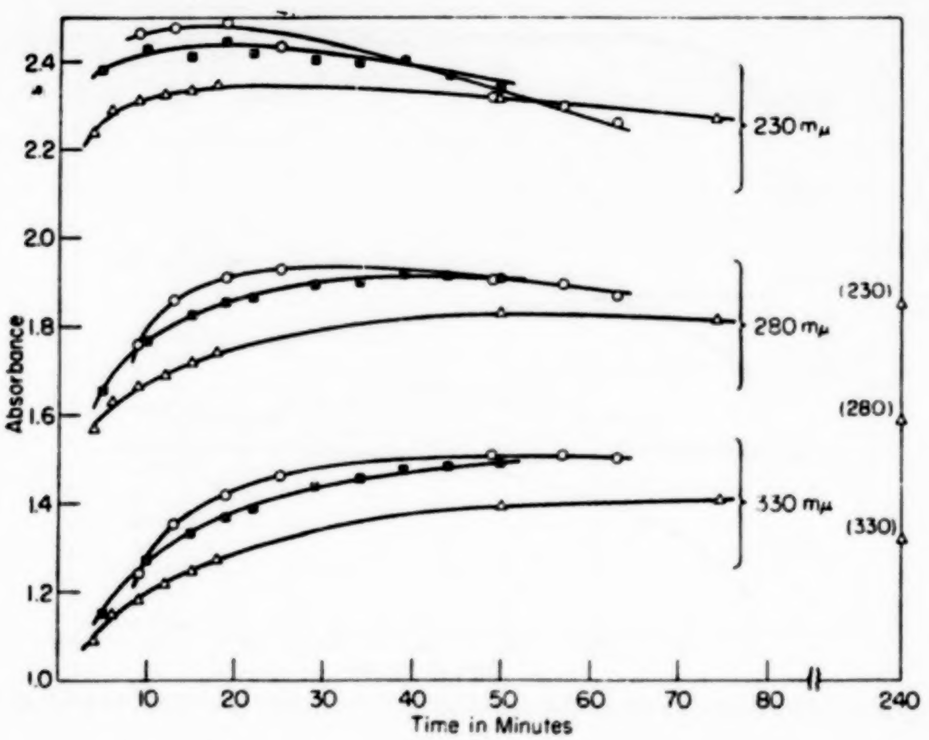

Fig. 2. Effect of different percentages of ethanol on absorbance values as a function of time.
○ 0% ethanol
■ 10% ethanol
△ 20% ethanol

noticeably. At 280 mμ and 330 mμ, the increase in absorbance continued for a longer time before leveling off. The effect of the ethanol was to lower the initial values of the absorbances, and to cause a more gradual increase in their values. This resulted in a crossover of the 0% and 10% curves especially at the short wavelengths. The points shown at the righthand margin are absorbances of the sol containing 20% ethanol and were recorded 4 hours after precipitation. These values indicated that progressively smaller changes with time were occurring in the absorbance values for the longer wavelengths.

Earlier work[8] had shown that the use of a solution of barium chloride as recommended by TOENNIES AND BAKAY[10] instead of the solid reagent markedly lowered the sensitivity of the nephelometric measurements for the determination of sulfate. The slope of the nephelometric calibration curves was only 14 "nephelos" units per μg of sulfate when a solution of the reagent was used, whereas a slope of 25 was obtained with the solid barium chloride. Fig. 3 illustrates the striking difference in the absorbance resulting from the use of the two methods of precipitation with sols of barium sulfate which were otherwise identical. When an equal volume of a 0.178*M* solution of barium chloride was mixed with a solution of 20.0 μg per ml of sulfate (each solution containing 20% ethanol), the absorbance readings were constant from 3 to 15 minutes after mixing and then slowly decreased. This is contrary to the behavior observed for the sols produced by solid barium chloride which showed a pronounced increase in absorbance for the first 20 minutes and, at the longer wavelengths, a slower increase for the next hour. Equally obvious when a solution of barium chloride reagent was used was the lesser dependence of the absorbance on the wavelength which resulted in much lower absorbance values at 230 mμ.

In view of the fact that the present study, as well as the previous nephelometric

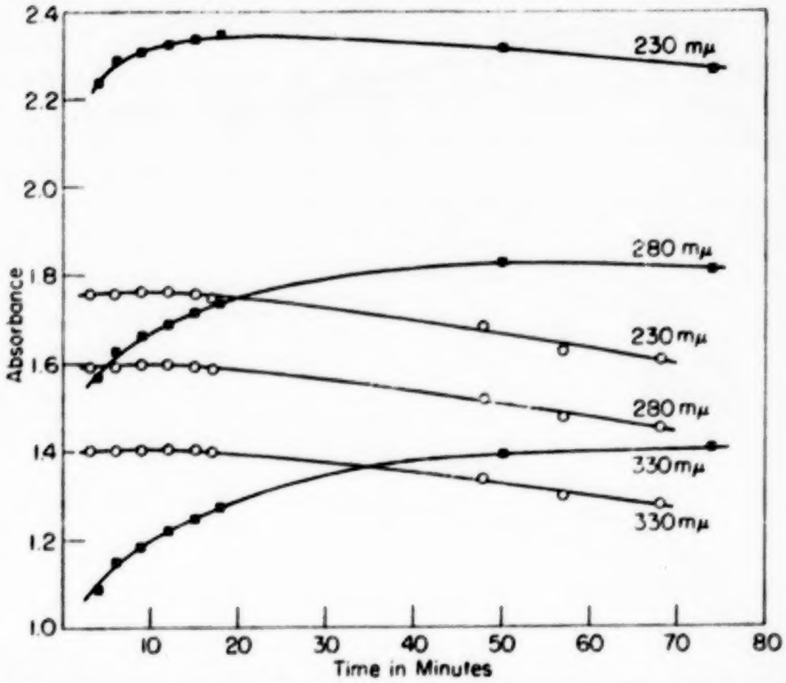

Fig. 3. Comparison of absorbance values obtained by two different methods of adding barium chloride.
■ solid
○ solution

one[8], was carried out in a room whose temperature was controlled to 24° ± 1° C, it was deemed advisable to examine the effect of changing the temperature of the solution at the time of precipitation to 15° C and to 35° C. Because much of the nephelometric work had been done on concentrated (about 1M) solutions of foreign salts[8], solutions which contained 10.0 μg per ml of sulfate, and 1.00M calcium chloride were chosen in order to facilitate comparisons.

Fig. 4 shows that the maximum difference between the absorbance values at two different temperatures, after the same time, was only about 5% over a range of 20° C, which is quite acceptable for most analytical purposes. However, the magnitude of the change differed with the wavelength, being smaller at longer wavelengths. The differences in absorbance values were not much greater then the experimental variation encountered at a single temperature upon redetermining the spectra for replicate samples at 24° C.

A comparison of the curves in Fig. 4 with those in Fig. 3 (for solid reagent) shows that the presence of calcium chloride in the solution markedly increased the stability of the sols, though their absorbances were decreased by about 20%. As will be pointed out later, this decrease was only about one-third of that observed nephelometrically.

Interpretation of spectral data

Observations of absorbance as a function of wavelength have been used by BARNES AND LAMER[1] for determining the particle size of sulfur sols, and involves a comparison of experimental data with theoretically calculated curves. However, the applicability of the comparison is limited to particles of spherical or nearly spherical shape[2]. Therefore, because the shapes of particles of barium sulfate produced by typical precipitation are non-spherical[11], and because nothing was known about the form of the distribution of particle sizes to be expected with the polydispersed sols of

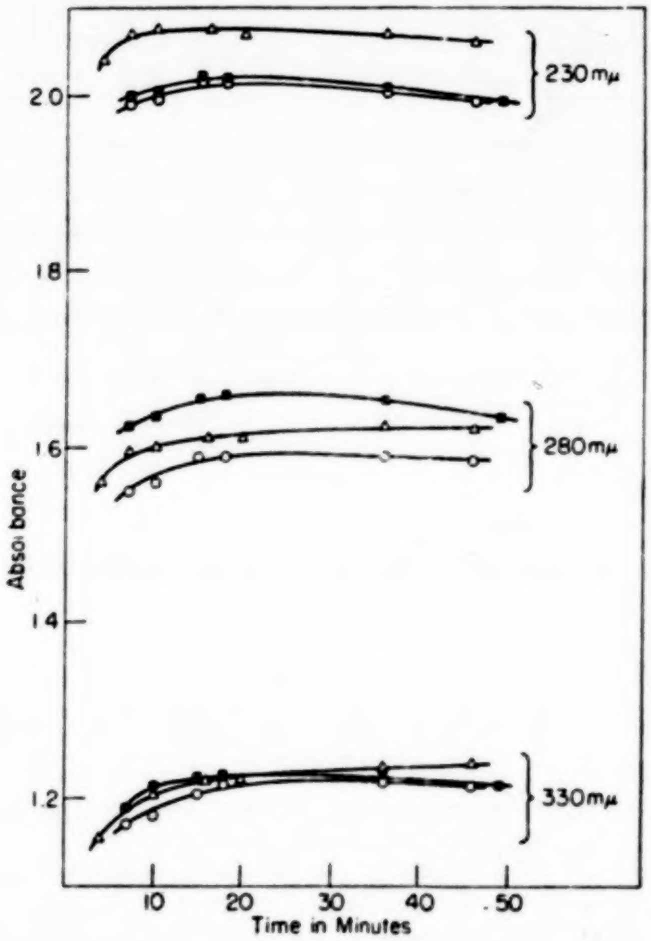

Fig. 4. Effect of temperature on absorbance values of sols produced in solutions containing 1.00*M* calcium chloride as a function of time.

△ 35°
○ 24°
■ 15°

barium sulfate obtained in this investigation, no attempt was made to calculate the values of average particle size from the absorbance data. Furthermore, in order to obtain data for comparison with the more readily calculable values from light-scattering theory, a low ratio of particle diameter to wavelength should be used. This would appear to require the use of wavelengths longer than the ultraviolet.

Heller and Vassy[5] have suggested that the change of relative particle size in an inorganic colloidal sol can be followed as a function of time from the slopes obtained by plotting for successive spectra the logarithm of the absorptivity against the logarithm of the reciprocal of the wavelength. When this type of plot was made for each of the spectra taken with a particular barium sulfate sol, the resulting curves were practically linear over the range of wavelengths from 230 mμ to 330 mμ. The average slope of each log plot was estimated by drawing a straight line between the points at 260 mμ and 300 mμ. Fig. 5 shows the slope of each log plot as a function of time, and each curve represents the kinetics of the changes in relative average particle size for each sol. As the average particle size becomes larger, the slope of the log plot decreases, *i.e.*, the absorbance becomes less dependent upon the wavelength.

Curve 1, taken from the spectra obtained for the barium sulfate sol produced with solid reagent in 20% ethanol, shows that there was a rapid change in average particle size during the first 30 minutes. Curve 5, plotted from the spectra of sols resulting from the use of solution reagent, may be compared directly with Curve 1

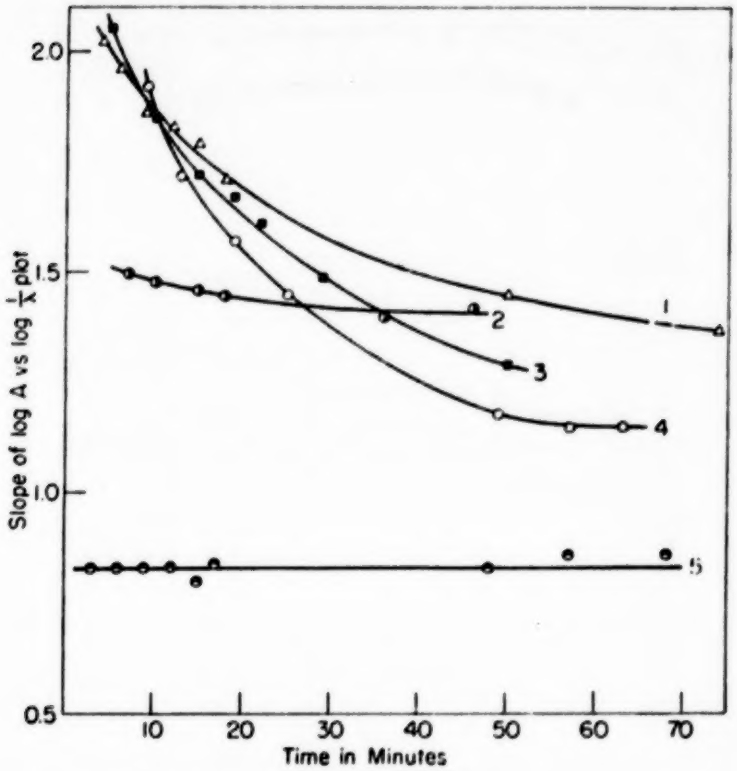

Fig. 5. Kinetics of changes in relative average particle size.
1. △ 20% ethanol, solid reagent
2. ◑ 20% ethanol, 1.00M $CaCl_2$, solid reagent
3. ■ 10% ethanol, solid reagent
4. ○ 0% ethanol, solid reagent
5. ◓ 20% ethanol, solution reagent

Refractive indices for these solutions are 1.34_4, 1.37_0, 1.34_2, 1.33_8, and 1.34_4 for curves 1-5 respectively.

because the final chemical composition of each solution was identical. It is evident that the average particle size produced by the use of the solution of barium chloride was much larger than that produced by the use of crystals. Furthermore, practically no change in average particle size occurred with time as a result of using the solution of barium chloride, whereas the use of the solid reagent resulted in a rapid increase in the average particle size during the first 30 minutes. Although the slope of Curve 5 was constant with time, Fig. 3 shows that the absorbance values decreased slowly but uniformly at all three wavelengths after the first 15 minutes. This would seem to indicate that settling of the particles rather than an increase in average particle size was occurring in these solutions.

Curve 2 shows that 1.00M calcium chloride greatly reduced the rate of increase of the average particle size. The fact that the magnitude of the slopes of this log plot fell below those of Curve 1 cannot be attributed unambiguously to a larger average particle size because of the difference in the refractive indices of the solutions — and possibly in the refractive index of the solid barium sulfate because of coprecipitation from the concentrated solutions of calcium chloride.

Curves 3 and 4 were calculated from the spectra for sols precipitated in the presence of 10% and 0% ethanol respectively. Together with Curve 1, for 20% ethanol, these curves show that the rate of change of particle size increased with decreasing alcohol content. Because of the small differences in the refractive indices, one is also relatively safe in extending the interpretation of the curves to a comparison of the relative average particle sizes in the three solutions.

Relationship between absorbance and concentration of sulfate

The large absorbance resulting from a sol produced from 10.0 μg per ml of sulfate suggested the possibility of determining sulfate by its apparent ultraviolet absorption. Furthermore, a comparison of Figs. 3 and 4 indicated that the presence of 1.00*M* calcium chloride did not decrease the absorbance of the solutions nearly as much as it did the nephelometric reading (from 25 to 10 nephelos units per μg of sulfate[8]). As a result, as shown in Fig. 6, calibration curves were established at three wavelengths (230 mμ, 280 mμ, and 330 mμ) with a series of solutions covering a concentration range from 2.5 to 10.0 μg per ml of added sulfate. Each point used to establish the curves was obtained 30 min after precipitation, and was the average of duplicate measurements. The range of the duplicates is indicated on the figure. These same solutions when read on the nephelometer produced values which agreed, within the previously reported limits, with the earlier data[8].

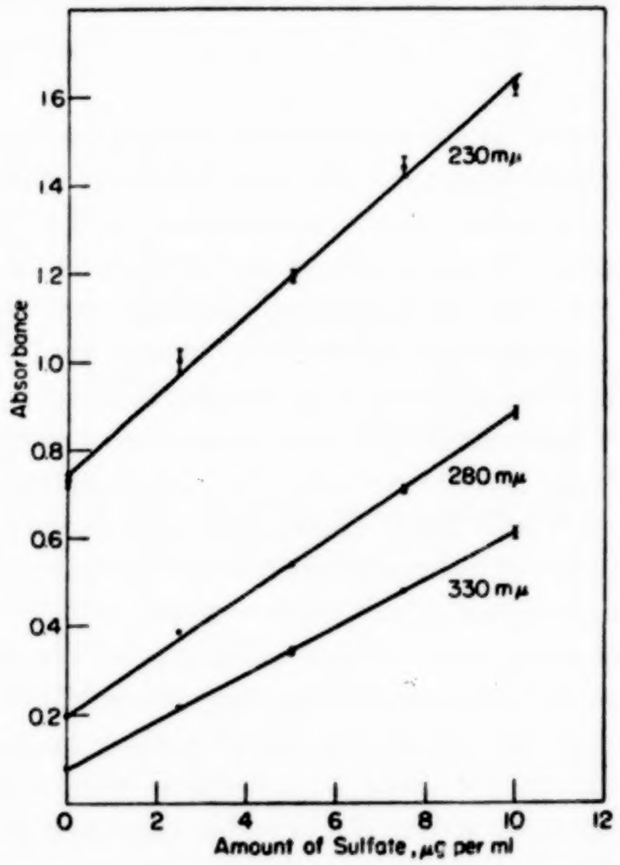

Fig. 6. Calibration curves at three wavelengths for 0-10 μg per ml of sulfate in 1.00*M* calcium chloride and 20% ethanol.

To explore further the reproducibility of the measurements, five replications of the absorbance measurements were made at sulfate concentrations of 5.0 μg per ml and 10.0 μg per ml for each wavelength. Table I shows the average values obtained after subtracting the blank readings. It is evident from a consideration of Fig. 6 that the slope of the calibration curve at 230 mμ, though greater, is less certain than at the longer wavelengths.

A constant slit width was maintained at each wavelength for the readings used in establishing a particular calibration curve. However, it was found that the readings were quite independent of the slit width so that any slit width, which would permit the instrument to be balanced against the reference cell, could be used. Furthermore,

TABLE I

CORRECTED FOR THE BLANK, ABSORBANCE READINGS, OF FIVE SAMPLES AT EACH OF TWO CONCENTRATIONS OF SULFATE

Sulfate μg per ml	5.0			10.0		
Wavelength in mμ	330	280	230	330	280	230
Average absorbance	0.263	0.343	0.459	0.539	0.686	0.887
Standard deviation of absorbance	0.005	0.003	0.011	0.010	0.010	0.016
Coefficient of variation of absorbance	1.9	0.9	2.4	1.9	1.5	1.8

it was shown that adjustment of the wavelength setting on the Beckman from either the high or low wavelength direction did not influence the absorbance readings.

It is evident from a comparison of the absorbance values taken on the Cary with those taken on the Beckman (Figs. 2 and 6) that the same solutions produced much larger readings on the Cary even though those readings were referred to a true blank, whereas the Beckman values were referred to water and therefore included the absorbance of the blank. This difference is undoubtedly due to instrument design. LOTHIAN AND CHAPPEL[12] have indicated how absorbance readings depend upon the solid angles through which the source and the detector view the sample. Higher absorbances are obtained when these angles are only a very few degrees removed from 0°. Because the amount of light scattered in the forward direction will be greater for larger particles, the smaller absorbance values obtained with the Beckman indicate that its receiver may view a large solid angle. The presence of more stray light in the Beckman could also contribute to such a difference.

The absorbance readings for 0.0 μg per ml of sulfate in Fig. 6 can be accounted for by the presence of the soluble inorganic salts as shown in Table II. As will be mentioned later, this additivity will make possible the analysis of general unknowns.

TABLE II

ADDITIVITY OF ABSORBANCES OF THE COMPONENTS OF THE BLANK

Wavelength in mμ	330	280	230
Absorbance of 1.00M $CaCl_2$	0.067	0.174	0.671
Absorbance of 0.089M $BaCl_2$	0.008	0.022	0.068
Calculated total	0.075	0.196	0.739
Observed total	0.074	0.197	0.734

Comparison of absorbtimetric and nephelometric data

In order to explore further the effect of the concentration of ethanol on the stabilities of the sols, a brief nephelometric study was made covering the range from 0-60% by volume. The data in Fig. 7 were obtained on solutions which contained 10.0 μg per ml of sulfate but no foreign salt, the presence of which would have tended to stabilize the readings. Ten minutes after the addition of the solid barium chloride, all the curves decreased with time. In general, the rate of decrease for the "nephelos" reading was smaller for larger concentrations of ethanol, as well as the magnitude of the reading. The solution containing 10% ethanol proved to be an exception to the latter observation by producing the highest "nephelos" values. The 20% ethanol solution was also an exception for time intervals greater than 80 minutes, the point at which it crossed the 0% curve.

A comparison of the nephelometric data in Fig. 7 with the absorbance-time curves in Fig. 2 for 0%, 10% and 20% of ethanol shows no simple correlation. It is apparent that up to 30 minutes after precipitation, the solution containing no ethanol had the highest absorbance values at all three wavelengths. Furthermore, the absorbance of the solution increased long after the 90°-scattered light began to decrease. The closest correlation between the nephelometric and the absorbtimetric data occurred at 230 mμ.

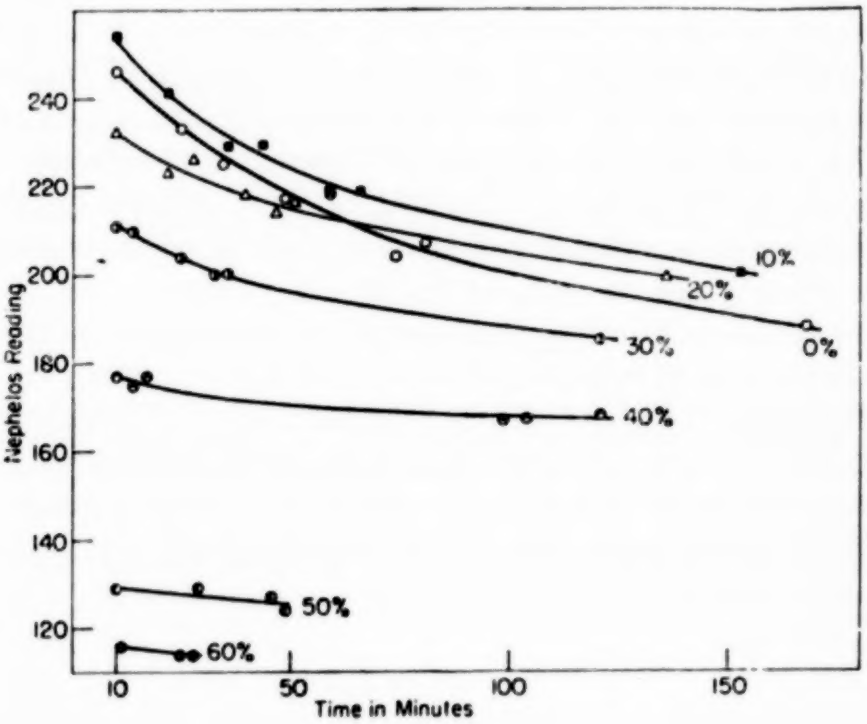

Fig. 7. Effect of different percentages of ethanol on nephelometric values as a function of time.

However, qualitative agreement was obtained when the rates of decrease of the nephelometric values were compared with the rates of increase of the relative average particle sizes calculated from the absorbance-time measurements. As shown by a comparison of Fig. 7 with Fig. 5, the least stable nephelometric readings were obtained on the solutions containing the least amount of ethanol, and these solutions showed the most rapid increase in average particle size with time. Likewise, the stability of the nephelometric measurements for barium sulfate sols in the presence of $1.00\,M$ calcium chloride[8] was directly attributable to the slow rate with which the average particle size increased. Furthermore, the very striking difference between the spectra obtained from the sols precipitated by means of a solution of barium chloride and those precipitated by solid crystals confirmed the distinct difference which had been observed nephelometrically. Use of the solution of reagent resulted in an initial average particle size which was relatively much larger than that obtained when solid reagent was used. Thus, the difference in the nephelometric slopes obtained by the two precipitation techniques (14 "nephelos" units per μg of sulfate for the solution of barium chloride; 25 "nephelos" units per μg of sulfate for the crystals) was the result of a decrease in the amount of 90°-scattered light and an increase in the forward scattering resulting from the larger average particle size.

Although the stabilities of the absorbance readings were greater when precipitations were made by mixing solutions rather than by dissolving solid reagent, one should not infer that the reproducibilities of the former were better. In fact, the opposite has been shown to be true[8]. The reproducibility was even poorer when the sulfate solutions contained high concentrations of foreign salt.

Of practical importance was the fact that absorption measurements in the ultraviolet region provided sufficient sensitivity to sols of barium sulfate to suggest the possible use of such measurements as a substitute for nepehelometry. The present paper indicates that absorbance could indeed be measured on very dilute sols but that larger volumes of solution were required for absorbance measurements in order to obtain comparable sensitivities. A coefficient of variation of approximately 1.7% for a level of 10.0 μg per ml (see Table I) was essentially the same as that previously reported for the nephelometric procedure[8]. However, absorbance measurements were advantageous in the presence of 1.00*M* calcium chloride because the reading for 10 μg per ml of sulfate was 80% of the value obtained in its absence. Nephelometrically, the reading fell to 40% of its former value.

An evaluation of the effect of the temperature of the solution on the nephelometric measurements of the sols of barium sulfate formed in the presence of 1.00*M* calcium chloride, was also made. The readings (in nephelos units) were 101.2 at 35° C, 96.0 at 24° C and 94.2 at 15° C. This overall change amounted to about 7% and agreed well with the temperature effect observed for absorbance measurements at the shorter wavelengths. With either nephelometric or absorbtimetric measurements, changes of ±5° C are not important.

DISCUSSION

The sensitivity of turbidimetric measurements in the ultraviolet region, using 10-cm cells, is sufficiently great to permit the measurement of sulfate concentrations which are usually handled nephelometrically. If this technique were to be used for the determination of sulfate, the interference of chemically absorbing species would have to be determined. It is possible, in the presence of low levels of absorbing species, that an analysis could be accomplished by measuring first the absorption of the sample solution before the addition of barium chloride and then the change in the absorption upon formation of the precipitate. Assuming the additivity of absorbances to be valid, the absorbance of the blank could be estimated by determining, in addition, the absorbance of the barium chloride (in the solvent mixture used) and adding it to the absorbance of the solution before the precipitation, as was done in Table II. Finally, the change in the absorbance per μg of sulfate, *i.e.*, the slope of the calibration curve, could be determined by the method of standard addition.

In some cases, a more direct estimation of the blank could be made by precipitating and filtering off the barium sulfate and then measuring the absorbance of the solution. However, in order to use this procedure, one would have to be certain that the filtering medium did not alter the solution itself and that the suspension was completely removed by the filtration.

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SUMMARY

Absorbance measurements in the ultraviolet have been shown to be useful for following changes with time in the average particle size of barium sulfate sols. The effects of the method of adding the barium chloride, a change in the temperature, the presence of 1.00*M* calcium chloride and the percentage of ethanol in the solution have been examined as a function of time. By measuring the apparent absorbance of barium sulfate sols in 10 cm cells, sulfate can be determined in the range of 2.5-10.0 μg per ml. This is a range which, in the past, has had to be handled by nephelometry.

RÉSUMÉ

Des mesures de l'absorption dans l'ultra-violet ont été effectuées pour suivre l'évolution de la grosseur moyenne des particules des sols de sulfate de baryum. L'influence de la méthode d'addition du chlorure de baryum, d'un changement de température, de la présence de chlorure de calcium 1.00*M* et de la concentration en alcool éthylique dans la solution a été examinée en fonction du temps. En mesurant l'absorption apparente des sols de sulfate de baryum dans des cuves de 10 cm, on peut doser des quantités de sulfate allant de 2.5 à 10 μg par ml. Ce sont là des concentrations qui, par le passé, devaient être mesurées par néphélométrie.

ZUSAMMENFASSUNG

Es wurden Ultraviolett-Absorptionsmessungen ausgeführt, um das Zunehmen der mittleren Teilchengrösse von Bariumsulfatsolen zu verfolgen. Der Einfluss der Zugabemethode des Bariumchlorides, einer Temperaturänderung, der Gegenwart von 1.00*M* Kalziumchlorid und der Konzentration an Äthylalkohol in der Lösung wurde in Funktion der Zeit untersucht. Wenn man die scheinbare Absorption der Bariumsulfatsole in einer Zelle von 10 cm misst, kann man Sulfatmengen in der Grössenordnung von 2.5 bis 10 μg per ml bestimmen. Das sind Konzentrationen, die bisher durch Nephelometrie gemessen werden mussten.

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THE DETERMINATION OF MICROGRAM QUANTITIES OF FLUORIDE
IV. THE USE OF THE ALUMINIUM-ERIOCHROMECYANIN COMPLEX

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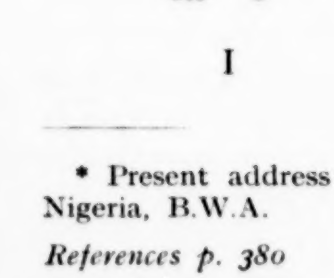
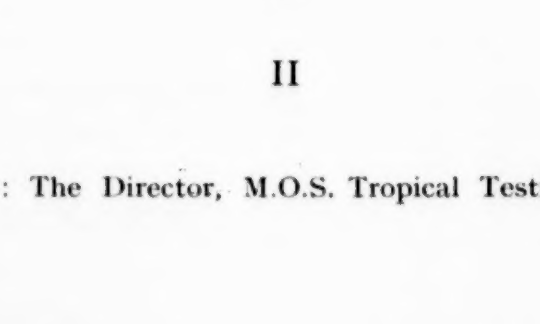
INTRODUCTION

The determination of fluoride in microgram amounts is of necessity carried out by means of a secondary effect since the element itself forms no known suitable coloured ions or complexes. Most successful methods for fluoride determination have been based on the destruction by fluoride of a coloured complex, the fading of coulour so produced being in many cases proportional to the concentration of the ion. In a previous paper[1,2] a method for determining fluoride using the complex between aluminium and haematein was described. In this paper it was mentioned that the aluminon-aluminium complex also showed a similar but very much less sensitive effect. From this work it was clear that an even more sensitive method could be developed if a dye aluminium complex of sufficiently high molecular absorbancy and a sensitivity to fluoride equal to that of the aluminium-haematein complex could be found. Consideration of the structure of haematein(I) and auramine tricarboxylic acid (aluminon)(II) indicated that a compound containing a structure of the type III would be likely to form a suitable complex with aluminium, type III being the essential component common to both I and II.



I



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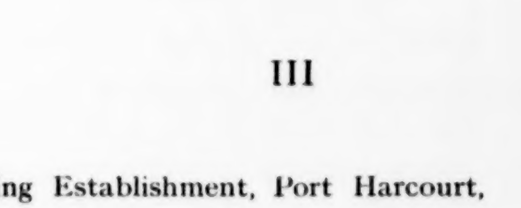

III

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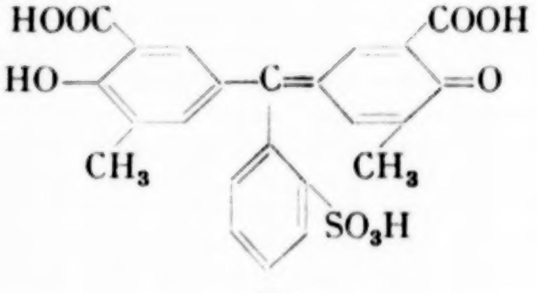
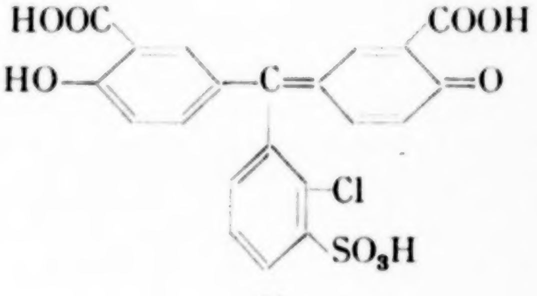
Two dyestuffs which possess this structure have been recently used in connection with the determination of fluoride, namely eriochromecyanin R (IV) which was used by Thrun[3] as the aluminium lake, by Megregian[4] as the zirconium lake and by Saylor and Larkin[5] as an indicator in the titration of fluoride with aluminium chloride, and chromazurol S (V) which was used by Milton[6] as the indicator in titration of fluoride with thorium nitrate. Thrun's method used far too great a quantity of dye and the sensitivity appeared to be disappointingly low, but that of Megregian which was published after the completion of the present work is of the order of sensitivity expected. The molecular absorbancies for the aluminium complexes of the four dyes (I, II, IV, V) have been determined and are shown in Table I. The figures indicated that both eriochromecyanin and chromazurol S should be superior to haematein for the determination of fluoride.



IV



V

TABLE I

Aluminium complex with	*Molecular absorbancy*
Aluminon	12,000
Haematein	33,000
Chromazurol S	44,000
Eriochromecyanin R	88,000

Preliminary experiments indicated that in fact the chromazurol complex was only a little more sensitive to fluoride whereas the eriochromecyanin R complex was at least three times more sensitive than the haematein complex.

The use of eriochromecyanin as a reagent for aluminium was fairly extensively studied some twenty years ago by Eegriwe[7], by Alten[8,9], by Millner[10] and by Richter[11,12], who also made some attempt to determine fluoride with the aluminium lake. The findings of these authors indicated that pH control was critical and that at least two forms of eriochromecyanin existed, one of which reacted readily with aluminium and the other which did not react or only very slowly. A spectrophotometric study of the eriochromecyanin and its aluminium complex at various pH's was therefore undertaken. Previous work on dye-aluminium systems[1,2] coupled with the findings quoted by German workers[7-12] indicated that a pH in the region of 4.2-5.0 would be most suitable for developing a method for fluoride determination and special attention was given to this range of pH in the present investigations.

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EXPERIMENTAL

From the previous work with haematoxylin[1] the approximate concentration of aluminium required for a method for determining microgram amounts of fluoride was known and this governed the amounts of the other reagents to be used. Preliminary experiments showed that the eriochromecyanin was quite stable at pH 2 but in the region 4.0-6.5 it was unstable, and that the form in which it was present was different since the absorption peak changed from 4800 Å to 5200 Å. In view of this behaviour the dye was kept in solution which was $0.01\,M$ with respect to hydrochloric acid. The peak of the aluminium eriochromecyanin complex was found to lie at 5350 Å and the complex in contradistinction to dye alone was quite stable. Fig. 1 shows spectra of dye alone at pH 2 and complex at pH 4.6.

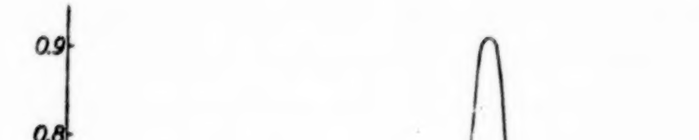

Fig. 1. Spectra of eriochromecyanin (a) and the eriochromecyanin-aluminium complex (b).
(a) Eriochromecyanin at pH 2 $3.7\cdot10^{-5}M$.
(b) Eriochromecyanin-aluminium complex at pH 4.5 $1.64\cdot10^{-5}M$.
Spectra plotted on a Unicam Spectrophotometer using a 1 cm cell.

Addition of various amounts of aluminium to a fixed amount of the eriochromecyanin showed that no further colour was produced by increasing the aluminium concentration when the ratio of dye to aluminium in the complex was two. Job's method of continuous variation gave the same result.

Detailed studies on the effect of pH on the dye, and on the dye aluminium complex were carried out as follows.

200 ml of water and 1 ml of concentrated acetic acid and 10 ml of $2.5M$ hydrochloric acid were placed in a beaker giving a pH of 1.01. 555 μg of aluminium (as aluminium ammonium sulphate) and 9 ml of eriochromecyanin (0.25% in $0.01\,M$ HCl) were added. The pH was adjusted to the desired value, using a pH meter, by the addition of $1.8M$ ammonium hydroxide and the absorbancy measured in a 0.1 cm cell at 5350 Å after each addition, the values obtained being corrected for volume changes. A similar experiment without the addition of the aluminium was also carried out.

The results (shown in Fig. 2) confirm the findings of previous authors that satisfactory complex formation takes place at pH between approximately 4.2 and 7.0 and that the intensity of the residual eriochromecyanin colour diminishes towards the higher pH values.

Now for a satisfactory method of determining fluoride the complex must not be too stable and the rate of the reaction shown in Equation (*a*) must not be too slow.

Complex $\rightleftharpoons$ eriochromecyanin + Al (*a*)

These conditions are likely to be fulfilled at pH values which are not quite optimum for complex formation, *i.e.*, between 4.0 and 5.0 and between 6.8 and 7.2. Obviously the higher values of pH are unsuitable as

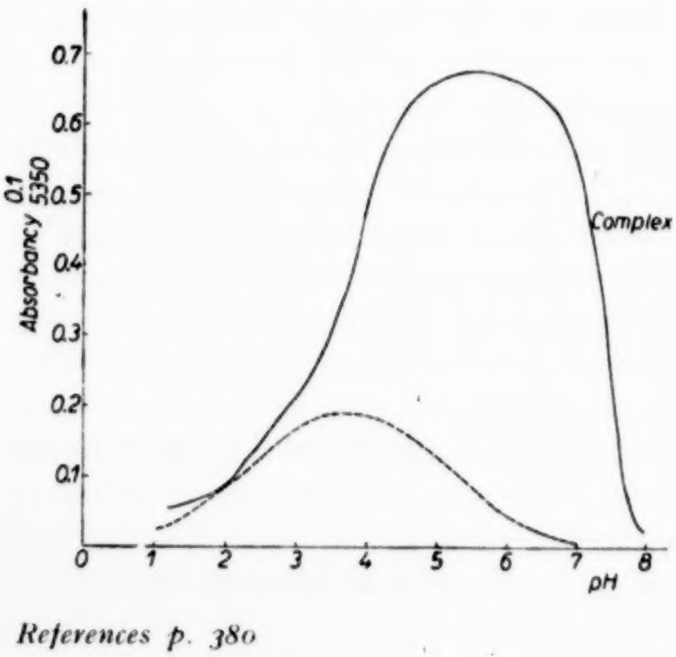

Fig. 2. Variation of complex formation with pH.
Dye alone — — — — — —
Complex ————————

aluminium may tend to precipitate and a pH within the lower of the suggested ranges has been chosen.

An attempt was then made to determine fluoride at pH 4.9 (the value already found satisfactory in the case of the aluminium-haematoxylin method) using a solution of complex prepared in the manner already described. The effect of fluoride on the complex was, however, very slow probably due to the slow rate at which the system came to equilibrium; nevertheless the effect produced after 12-16 hours was considerably greater than the effect obtained with the aluminium-haematein complex. The time required was however too long for a successful method and attempts were made to shorten the time taken for the system to approach equilibrium. Reduction of pH, as expected, produced some improvement but to shorten the time to one hour at room temperature it was necessary to go down to a pH of 4, at which value the equilibrium of Equation (*a*) was so far over to the right that the sensitivity of the method was considerably impaired.

The position at this stage may be summarized as follows:

(a) Eriochromecyanin solutions could be kept satisfactorily at low pH (ca. 2.0).
(b) Stock solutions of eriochromecyanin-aluminium complex could be prepared which were stable indefinitely.
(c) Reactions between such stock solutions and fluoride ions were of great sensitivity but the time factor was unsatisfactory.

The obvious way of increasing the rates of reactions involved between fluoride and the dye-aluminium complex was to raise the temperature and experiments at higher temperatures were therefore undertaken.

Effect of temperature on the fluoride-aluminium-eriochromecyanin system

It was found that when solutions containing various amounts of fluoride and a fixed amount of stock solution (prepared in a manner similar to that described in the section headed "Method") were heated at 35° C a reproducible reaction occurred in solutions containing approximately 22 µg Al/50 ml and that the reaction was substantially complete in about two hours. It was found also that provided the concentration of acetate (used as buffer) was low the blank containing no fluoride was also stable. Unheated blanks were stable also in the presence of a somewhat higher concentration of acetate.

The experiments were repeated at 60° C when it was found that reaction was complete in 15 minutes. In order to avoid complications arising from different rates of heating and cooling, all solutions were made up to a constant volume before heating and cooled down to near room temperature in a cold water bath.

A test method in which fluoride was added to stock solution of complex at pH 4.9, the solution made up to standard volume, heated at 60° C for 15 minutes and then cooled in cold water to room temperature gave good reproducible results but the response to fluoride was not linear, but a similar experiment at pH 4.5 resulted in considerable improvement and calibrations in these conditions approximated very closely to a straight line.

Determination of test samples of fluoride under these conditions gave recoveries of 93% (Table II).

TABLE II

RECOVERY OF FLUORIDE (µg) FROM H_2SO_4 SOLUTION BY DISTILLATION AND DETERMINATION WITH ALUMINIUM ERIOCHROMECYANIN COMPLEX

Fluoride added	*Fluoride found*	*% Recovery*	*Fluoride added*	*Fluoride found*	*% Recovery*
0	0	—	50	48	96
0	0	—	60	54	90
0	0	—	80	72	90
0	0	—	100	92	92
15	14.1	94	100	93	93
30	29	96	100	93	93
50	46	92			

Mean Recovery 92.7%

Effect of change of ionic strength on the complex

Since many distillates for fluoride determination contain large quantities of free acid it is necessary to ensure that the effect of an increase in ionic strength in a solution of complex will be small. Experiments showed that increasing the ionic strength of a solution of eriochromecyanin-aluminium complex resulted in a decrease in complex concentration which was approximately proportional to $\sqrt{I}$ for a small increase in I (Table III). The pH control, of course, was also affected, a significant decrease in pH occurring in the solutions of higher ionic strength. An obvious remedy was to increase the ionic strengths of all solutions. This was done by making the stock solution 0.5*M* and the buffer solution 2*M* with respect to ammonium chloride. Attempts were made to make the stock solution 1*M* with respect to ammonium chloride but these resulted in some precipitation of the complex. The addition of salt resulted in a decrease in total complex concentration which was compensated by increasing the amount of stock used in the fluoride determination.

TABLE III

THE EFFECT OF IONIC CONCENTRATION I ON THE ABSORBANCY OF ERIOCHROMECYANIN-ALUMINIUM COMPLEX SOLUTIONS (STANDARD STOCK SOLUTION USED)

I	$\sqrt{I}$	Salt KCl △ Absorbancy	pH	Salt NH_4Cl △ Absorbancy	pH
0.004	0.0632	0	4.56	0	4.56
0.084	0.29	0.107	4.47	0.128	4.47
0.164	0.405	0.175	4.44	0.214	4.43
0.324	0.57	0.261	4.42	0.314	4.40
0.644	0.8	0.328	4.40	0.419	4.36
1.28	1.13	—	—	0.463	4.32

The addition of salt to stock and buffer solutions also resulted in improved pH control. Recoveries of fluoride by distillation as hydrofluosilicic acid and determination using the new technique now gave recoveries close to 100% (Table IV).

TABLE IV

RECOVERY OF FLUORIDE (μg) FROM H_2SO_4 SOLUTION BY DISTILLATION AND DETERMINATION WITH ALUMINIUM-ERIOCHROMECYANIN COMPLEX USING SOLUTIONS OF INCREASED IONIC STRENGTH (0.8)

Fluoride added	*Fluoride found*	*% Recovery*	*Fluoride added*	*Fluoride found*	*% Recovery*
0	< 1	—	30	29	97
0	0	—	30	30	100
0	0	—	30	30	100
20	20	100			
30	30	100	35	36	103

Mean Recovery 100%

Effect of pH on eriochromecyanin

In parallel with the experiments on the effect of temperature and ionic strength an investigation into the behaviour of eriochromecyanin with pH and its reaction with aluminium under these conditions was started.

Two solutions of 0.01% eriochromecyanin were prepared by dilution of the 0.25% solution used for the method and the pH adjusted to 4.6 and 2.0 respectively. These solutions were diluted to 0.002% and the spectra recorded immediately using a Unicam spectrophotometer and 1 cm cells. Change of spectra were recorded with time over several weeks, the solutions being kept at room temperature (Fig. 3). It was found that the dye at pH 2.0 has an absorption peak at 4800 Å and this is perfectly stable, showing no change over a period of five months. The solution of dye at pH 4.6, which had an absorption peak at 5200 Å, underwent a rapid change (Fig. 3), the peak height falling off to less than half its original height in 24 hours (Curve D, Fig. 3). No further decrease in peak height at 5200 Å was detected even after five months; a spectrum plot gave a curve identical with D.

Further investigation of the eriochromecyanin at pH 4.6 showed that heating to 60° C increased the rate of decrease of absorbancy at 5200 Å but made no difference to the final figure obtained (Curve D). The rate of decrease was independent of dye concentration for solutions containing 0.002%-0.05% eriochromecyanin. When the pH of the solution of aged (faded) dye was changed from 4.6 to 2.0 and then restored to 4.6 it was found that the height of the absorbancy peak at

5200 Å had returned to its original value. The peak height proceeded to decrease with time as previously observed. This process of regeneration and decay of the original form of eriochromecyanin at pH 4.6 could be repeated indefinitely.

Freshly prepared dye at pH 4.6 reacted rapidly with aluminium giving a maximum absorbancy at the complex peak 5350 Å after ten minutes, whereas aged dye of the same pH reacted only very slowly, the reaction taking approximately eighteen hours to reach completion.

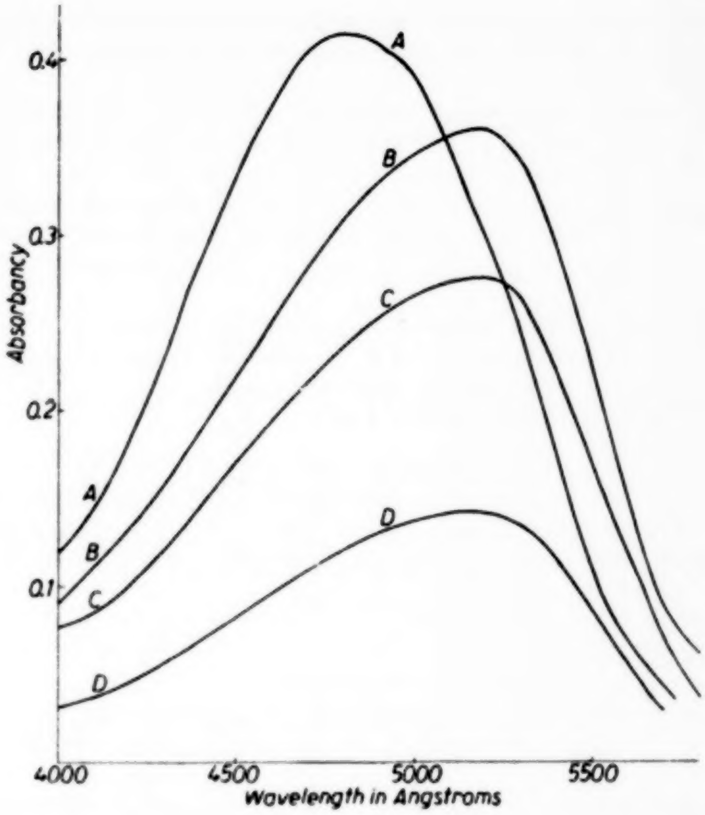

Fig. 3. Spectra of eriochromecyanin (0.002% solution).
A. pH 2.0
B. pH 4.6 Freshly prepared
C. pH 4.6 Age 6 h
D. pH 4.6 Age 24 h

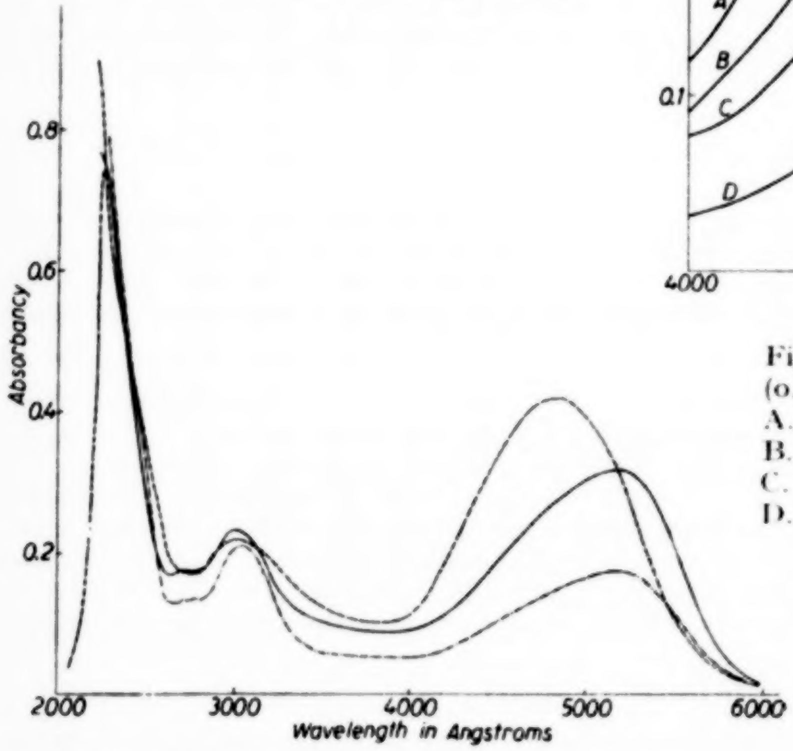

Fig. 4. Spectra of eriochromecyanin.
Freshly prepared 0.002% dye pH 4.6 ————
Aged 0.002% dye pH 4.6 — · — · —
0.002% dye pH 2.0 — — —

Complete spectra of the dye solutions at pH 2.0 and 4.6 were recorded on a Hilger Uvispec spectrophotometer using a one centimetre cell and the results are shown in Fig. 4.

The spectrum of the dye obtained by complete destruction of the aluminium complex by fluoride is shown in Fig. 5. The spectrum corresponds to that of an aged dye which has nearly completed the aging process, and on standing the absorbancy decreases to the expected figure (corresponding to curve D, Fig. 3).

METHOD

A. *Reagents*

(i) *Standard fluoride solution*
Dissolve 0.5525 g of sodium fluoride in water and dilute to 250 ml. Dilute 1 ml of this solution to 100 ml.
1 ml = 10 μg F.

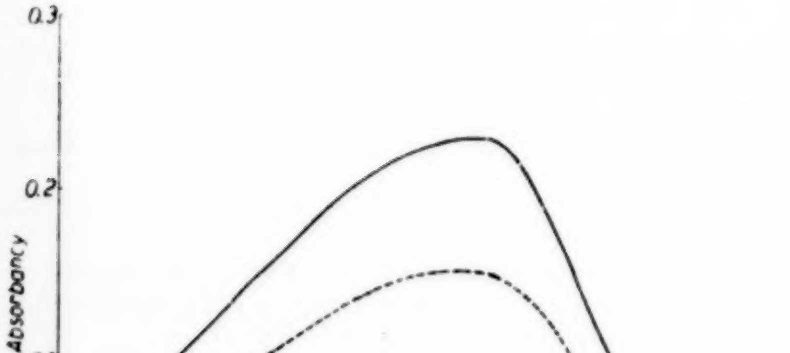

Fig. 5. Spectra obtained after complete destruction of complex by fluoride.
Spectrum recorded immediately ——
Spectrum recorded after 1 day - - - -

The purest available material should be used; that supplied by **Baker and Adamson** to A.C.S. specification is suitable.

(ii) *Standard aluminium solution*
Dissolve 1.867 g 'AnalaR' quality aluminium ammonium sulphate ($AlNH_4(SO_4)_2.12H_2O$) in water and dilute to 100 ml.

1 ml = 1.11 mg Al.

For use dilute 10 ml of the above solution to 100 ml.

1 ml = 111 μg Al.

(iii) *Eriochromecyanin solution 0.25%*
Dissolve 0.25 g of solid in 10 ml of $0.1M$ hydrochloric acid and dilute to 100 ml.

(iv) *Ammonium hydroxide 9M.*

(v) *Glacial acetic acid.*

(vi) *Buffer solution (pH 4.5)*
Dissolve 32 g 'AnalaR' quality ammonium chloride in 220 ml of water. Add 25 ml of glacial acetic acid and 7.5 ml of concentrated ammonia (sp.gr. 0.88). Cool to room temperature and adjust pH to 4.5 by further addition of ammonia using a pH meter. Dilute to 300 ml and filter.

B. *Procedure*

(a) *Preliminary treatment*
Separate the fluoride from interfering ions if necessary by distillation from sulphuric acid in the presence of silica according to the method of **Willard and Winter**[13]. Collect 160 ml of distillate. If a micro apparatus such as that described by **Horton, Thomason and Miller**[14] and by ourselves[15] is used, only 10-20 ml need be collected. Treat distillate as described below.

(b) *Treatment of distillates*

I. *For distillates of acid content equivalent to <1 ml $1M$ acid/150 ml*
This applies also to samples where distillation is not necessary, *e.g.*, water.

(i) Neutralize the distillate to phenolphthalein with $0.1M$ sodium hydroxide. Record the volume of the neutralized solution and the volume of alkali used.

(ii) Prepare a blank solution by neutralizing a volume of $0.1M$ sodium hydroxide equal to that used in step (i) with $0.05M$ H_2SO_4 using phenolphthalein as indicator. Dilute the solution to a volume equal to that of the neutralized distillate

II. *For distillates of high acid content*

(i) Add sufficient $9M$ ammonium hydroxide to the distillate to bring the pH to 7 and note the volume required. Add 1 ml of glacial acetic acid and adjust the pH to 4.5 by further addition of ammonium hydroxide, and again note volume used.

(ii) Prepare a blank solution by adding 1 ml glacial acetic acid to a volume of $9M$ ammonium hydroxide equal to the total amount used in step (i) and dilute to at least 120 ml. Add acid (of the kind present in the distillate) to bring the pH to 4.5. Dilute the solution to a volume equal to that of the neutralized distillate.

(c) *Determination of fluoride*

(i) Place a suitable volume of the neutralized distillate in a 50 ml flask and an equal volume of blank solution in a second 50 ml flask. Add 2 ml acetate buffer to each flask and mix well.

(ii) Into each flask pipette 15 ml aluminium-eriochromecyanin stock solution; make up to the mark with water and mix well.

(iii) Place flasks in a water bath at 60° C for 15 minutes. Cool to room temperature by immersion in a cold water bath.

(iv) Measure the difference between the absorbancies of the two solutions using light of wavelength 5350 Å. The Unicam spectrophotometer and a 1 cm cell are recommended for this operation but other suitable instruments may be used.

(v) Calculate the fluoride present by reference to a prepared calibration graph.

C. *Preparation of aluminium-eriochromecyanin stock solution*
To 450 ml water in a 600 ml beaker add in order the following, mixing well after each addition:

(i) 13.4 g ammonium chloride

(ii) 1 ml glacial acetic acid

(iii) 20 ml 0.25% eriochromecyanin solution

(iv) 10 ml standard aluminium solution (111 μg Al/ml)

Finally add 1.8M ammonium hydroxide to bring the solution to pH 4.5 using a pH meter. Make up to 500 ml and filter through a Whatman No. 1 paper. Add one crystal of thymol to prevent mould growth.

The stock solution should be allowed to stand for two or three days before use.

D. *Calibration*

(i) Into each of six stoppered measuring flasks (numbered 1-6) of 50 ml capacity pipette 2 ml of buffer solution (pH 4.5).

(ii) Add standard fluoride solution to the flasks to give fluoride content as follows: —

Flask No.	1	2	3	4	5	6
$\mu g\ F^-$	0	4	8	12	16	20

(iii) Add 30 ml of water to each.

(iv) Add 15 ml of aluminium-eriochromecyanin stock solution to each, make up to the mark with water and mix well.

(v) Place the flasks in a water bath at 60° C for 15 minutes.
Then cool to room temperature by placing in a bath of cold water.

(vi) Measure the difference between the absorbancy of each fluoride containing solution and that containing none, using a Unicam spectrophotometer and a 1 cm cell with light of wavelength 5350 Å.

(vii) Plot a calibration graph of the difference in absorbancy against fluoride concentration. Two typical calibrations are recorded in Table V.

INTERFERENCES

Since this method is basically the same as the aluminium haematoxylin method it is to be expected that the ions interfering with the present method would be the same. In general this is correct. In two cases, however, the effects are different, namely in the cases of nitrite and phosphate (H_2PO_4) where a concentration of 20 p.p.m. in both cases reduces the sensitivity of the method.

DISCUSSION

A. *The method*

The two typical calibrations shown in Table V and a series of recoveries under normal conditions of use shown in Table VI give a good idea of the accuracy and reproducibility of the method.

TABLE V

TYPICAL CALIBRATIONS FOR THE ALUMINIUM-ERIOCHROMECYANIN METHOD

$\mu g\ F^-$		0	4	8	12	16	20
$\triangle$ Absorbancy · 10^3	(a)	0	122	234	352	477	580
	(b)	0	116	241	347	485	570

The standard deviation of the method is just less than 0.3 at the 3 µg and 11 µg level and 0.68 at the 18 µg level, the overall standard deviation being 0.53. (These figures are taken from a statistical comparison of several methods for fluoride determination which will be fully discussed in Part VI of the present series of papers.) Taking double the standard deviation as giving a 95% probability of a positive result at the detection limit, 0.6 µg should be detectable in 50 ml of final solution. In the case of macrodistillation the amount of distillate after neutralization is of the order of 170 ml and about 30 ml of this can be used for determination; the sample therefore must contain a minimum of 3.6 µg of fluoride. In a macrodistillation

TABLE VI

TYPICAL RECOVERIES OF FLUORIDE (μg) BY THE ALUMINIUM-ERIOCHROMECYANIN METHOD

F^- added	*F^- recovered*	*F^- added*	*F^- recovered*
3	3.0	18	18.3
	3.1		18.4
	3.0		17.7
	3.1		17.9
	2.8		18.5
	2.9		18.1
	3.1		17.5
	3.2		17.7
	3.2		17.8
	3.2		17.9
5	5.0	30	30.0
			30.0
11	11.0		29.0
	10.9		
	11.4	40	40.0
	11.2		40.0
	10.8		40.0
	10.7		
	11.1		
	11.1		
	11.0		

apparatus 25 g of sample can easily be handled, giving us a limit of detection for fluoride of about 0.15 p.p.m. Using microdistillation where the whole distillate can be used — and in favourable cases 5 g of original sample — the limit of detection will be about 0.1 p.p.m.

In a recent paper MEGREGIAN[4] used the complex between eriochromecyanin and zirconium as a reagent for fluoride. His method possesses the advantage that heating is not necessary, but on the other hand the method is affected by sulphate and when this ion is present even in small quantities the amount must be known. MEGREGIAN states that he can determine fluoride in the range 0.00 to 1.40 mg of fluoride per litre with a standard deviation of ± 0.0163 mg fluoride per litre; the corresponding figures for the aluminium eriochromecyanin method expressed in MEGREGIAN's terminology as mg of fluoride per litre are, for a range 0.00–0.36 a standard deviation of ± 0.0100 and for a range 0.36–0.60 a standard deviation of ± 0.0230, the overall standard deviation being 0.0176.

Thus there is little to choose between the two methods. MEGREGIAN's is probably a little quicker to carry out since the heating and cooling required in our method is likely to add about 20 min to the time for a single determination but this would make very little difference where large numbers of samples were being handled; on the other hand the aluminium-eriochromecyanin method does not appear to be affected by sulphate.

Although MEGREGIAN mentions in his paper that complexes formed between aluminium and fluoride and zirconium and fluoride are $[AlF_6]^{-3}$ and $[ZrF_6]^{-2}$, such calculations as can be made from his figures indicate a ratio of one zirconium atom to about one and a half fluorine atoms, which is what we would have expected from the sensitivity of his method. Under the conditions of the aluminium-erio-

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chromecyanin method aluminium and fluorine appear to be combined in the ratio of 1:2. The question therefore arises as to the form in which the fluoride is combined with the aluminium (or zirconium), whether all the aluminium released from the complex reacts with fluoride to give compounds of the nature of $[AlF_y(OH)_{6-y}]^{-3}$ or whether species formed is $[AlF_6]^{-3}$ with the extra complex being destroyed to maintain some equilibrium between it and an aluminium hydroxide. We are at present investigating this problem further although from the work of BROSSETT[16] we would expect the formation of $[AlF_y(OH)_{6-y}]^{-3}$ (y having values from 1-6).

In the experiments on the fluoride-aluminium-eriochromecyanin system at elevated temperatures the question of the stability of the blanks arose. Completely stable blanks are not of course essential to a method provided they behave in the same way as the sample solutions. In the present case if any reaction involving fluoride (the variable) is virtually complete any subsequent changes in the solution will depend only on the decomposition of the free dye, since it has been found that the complex is quite stable under the conditions of use; and since the decomposition of free dye appears to be independent of the concentration, any slight instability arising from this should affect all readings equally and will therefore not affect the results if the initial conditions of the method are correct.

B. *Mechanism of reactions involved in the method*

The eriochromecyanin was chosen as a likely agent for use, as its aluminium complex, in the determination of fluoride because of its similarity to the basic structure which made haematein and aluminon possible reagents for the same purpose. Hence it would be expected that the reaction mechanisms involved in the present method should be similar to, or at any rate not contradictory to the explanation advanced in the case of haematein.

Any explanation of the mode of action of the eriochromecyanin-aluminium complex in the determination of fluoride must cover the following points:

(i) The ratio of dye to aluminium under the conditions used is 2:1.

(ii) A satisfactory complex is only formed in the pH region 3.5-7.5.

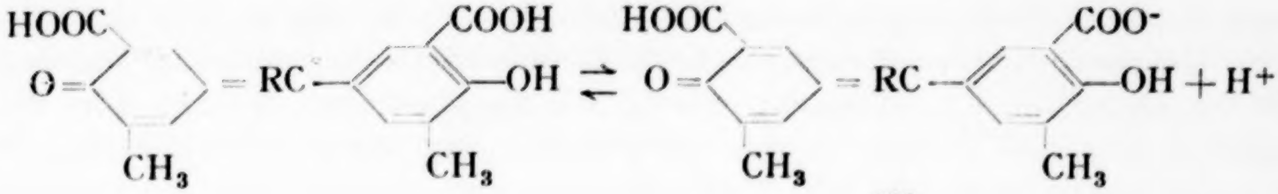
(iii) The form of the eriochromecyanin around pH 4.6 differs from that at pH 2 as judged by the absorption spectrum.

(iv) The form of eriochromecyanin existing around pH 4.6 is unstable and undergoes a change with time (aging).

(v) Eriochromecyanin freshly brought from pH 2.0 to pH 4.6 reacts rapidly with aluminium whereas after aging the reaction is slow and takes about 18 hours to complete.

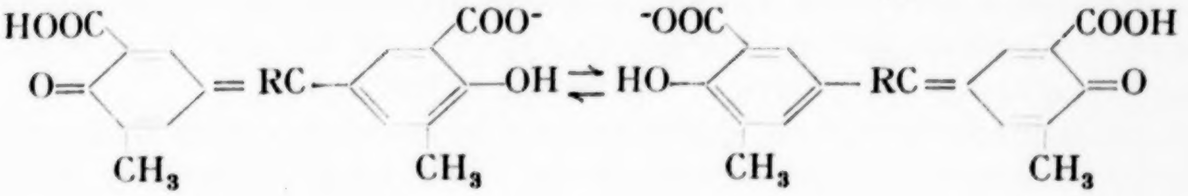
(vi) By taking aged eriochromecyanin to pH 2.0 and then returning the pH to 4.6 the active form of the dye is regenerated, and this process of aging and regeneration can be repeated indefinitely.

The following series of reactions is suggested as covering the above facts. The first stage (Equation 1) is represented by the ionization of the eriochromecyanin: R represents the phenylsulphonate group which is almost certainly completely ionized, this being the grouping which gives the dye its water solubility. The main resonance possibilities of the ion VI are indicated in Equation 2; it will be noted that the ion configuration is essentially the same configuration as that of the active ortion of the haematein ion as described in our previous paper[2].



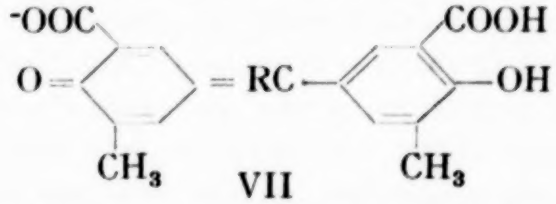
VI

(1)



(2)

It is probable also that the ion exists in the form



VII

but all these forms are regarded as equivalent, the remaining un-ionized hydrogen not necessarily being bound to the molecule at a specific point.

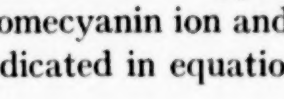
The second stage of the reaction would appear to be the formation of a chelate compound between the eriochromecyanin ion and the aluminium, which presumably takes place in two steps, as indicated in equation 3 (where R^- = eriochromecyanin ion)

$$2R^- + \text{Al (hydrated)} \rightleftarrows R^-.\,\text{Al (hydrated)} + R^- \rightleftarrows R_2^=.\,\text{Al (hydrated)} \qquad (3)$$

As a result of the formation of the complex the essential configuration of the ion is retained and the resonance possibilities are enhanced being extended through the aluminium over two molecules, this increased resonance results in the slight shift of the absorbancy peak of the complex and its high molecular absorbancy.

The form in which the aluminium reacts is of importance in deciding the exact nature of the reactions or series of reactions by which the complex is formed. From our previous work[2] and such rough calculation as can be made from BROSSETT's[17] latest work, although his conditions are not strictly comparable with our systems, the ion involved would appear to be $Al(OH)_2^+$ although the ion $(AlOH)^{+2}$ still remains as a possible alternative.

Of the possible structures for the complex only VIII which is similar to the proposed structure of the aluminium salicylate complex would appear from valency considerations to be tenable. This structure then would involve the addition of water



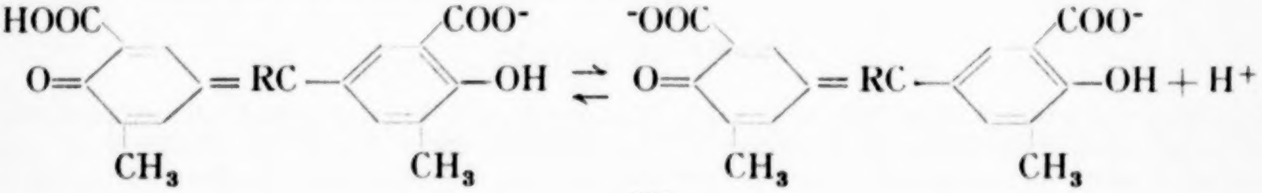
$$\left[R_2 \cdot Al\begin{smallmatrix}OH\\OH_2\end{smallmatrix}\right]^{-2} \qquad R = \text{eriochromecyanin ion}$$

VIII

if reaction took place through the $(AlOH)^{+2}$ ion and the addition of hydrogen ion in the case of the $Al(OH)_2^+$ ion. Unfortunately the present system provides no means of elucidating the problem, though other systems where the reactive dye ion is stable over a greater pH range may provide the answer.

The ageing of the dye to give a form which reacts only very slowly with aluminium provides a problem of some interest. It has been found (see Experimental) that over a range of concentration of 0.002 to 0.05% eriochromecyanin the rate of ageing of the dye is independent of the concentration. Hence any reaction explaining this ageing must be first order with respect to the dye and the dye ion, and since on a change of pH from 4.5 to 2.0 the reactive form of the dye is completely re-generated any such reaction must be readily reversible.

It is suggested that the cause of ageing is the slow further ionization of the eriochromecyanin ion according to Equation 4



(4)

IX

and that the ion so formed (IX) is not reactive towards aluminium. Whether any further reaction takes place is not known, but if so, Equation 4 remains the rate controlling step. It is significant that a rough plot of pH against amount of base added to a known quantity of the dye indicates that further ionization takes place in the range of pH in question. The fact that the rate of ageing of the dye, and the rate of complex formation between aged dye and aluminium are both of the same order at room temperature cannot be without significance and must result from the fact that the amount of dye ion formed (Eq. 1) ultimately controls both these reactions.

The reason for the limited pH range over which satisfactory complex formation occurs is due to a combination of two causes, first the range in which the eriochromecyanin ionizes to give a form suitable for reaction and secondly the pH range in which the aluminium exists as $Al(OH)_2^+$. Brossett's figures again indicate that in the region where complex ceases to be formed (pH 6.5-7.5) the amount of aluminium present as $Al(OH)_2^+$ will be small.

The destruction of complex by fluoride will follow the lines suggested in our previous paper[2] and since the rate of destruction is of the same order as the rate of ageing of the dye the resultant spectra will approach that of aged dye.

It is realized that this scheme for the mechanism of reaction is only tentative and that further work involving both the aluminium and zirconium complexes with eriochromecyanin and with chromeazurol S will have to be undertaken to fully elucidate the problem. Such work is being commenced but owing to pressure of other commitments it may be a considerable time before it can be finished and the suggested mechanisms have therefore been outlined in the present paper.

ACKNOWLEDGEMENT

The authors wish to thank Mr. A. S. Nickelson for his interest and encouragement during the course of this work.

SUMMARY

A spectrophotometric method for determining fluoride using the aluminium-eriochromecyanin complex is described. Fluoride in solutions free from interfering ions, or obtained by distillation as hydrofluosilicic acid is determined by its destruction of the complex, the amount destroyed being directly proportional to the fluoride content. The method will detect as little as 0.02 μg/ml of fluoride and with 0-20 μg in the final solution fluoride can be determined with accuracy of ± 0.6 μg.

A preliminary study of the aluminium-eriochromecyanin-fluoride system has been carried out and a tentative reaction mechanism suggested.

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RÉSUMÉ

Une méthode spectrophotométrique est décrite pour le dosage des fluorures, au moyen du complexe aluminium-ériochromecyanine. L'anion fluorhydrique en l'absence d'ions gênants, ou séparé par distillation comme acide fluosilicique, est dosé par destruction du complexe, la quantité décomposée étant proportionnelle à la quantité de fluorure. Cette méthode permet de déceler jusqu'à 0.02 μg/ml de fluorure. Des quantités de F^- allant de 0 à 20 μg peuvent être dosées avec une précision de ± 0.6 μg. Une étude préliminaire du système aluminium-ériochromecyanine-fluorure a été effectuée et on propose un mécanisme de réaction éventuel.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Methode beschrieben, um Fluorid mittels des Aluminium-Eriochromcyanin-Komplexes zu bestimmen. Das Fluorid-Anion wurde in Abwesenheit von störenden Ionen, oder abgetrennt mittels einer Destillation in Form von Fluorkieselsäure durch Zersetzung des Komplexes bestimmt. Die Menge, welche zerstört wurde, war direkt proportional der Menge an Fluor. Diese Methode erlaubt Fluormengen bis zu 0.02 μg nachzuweisen. Mengen von F^- zwischen 0 und 20 μg können mit einer Genauigkeit von ± 0.6 μg bestimmt werden. Es wurde eine Voruntersuchung des Systems Aluminium-Cyanin-Fluorid ausgeführt und ein möglicher Reaktionsmechanismus vorgeschlagen.

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A RAPID METHOD FOR THE DETERMINATION OF POLYOLS BY DICHROMATE OXIDATION, SPECTROPHOTOMETRIC MEASUREMENT OF Cr(III)

by

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In the course of the development of a procedure for the separation of several polyols from each other by anion-exchange chromatography of their borate complexes[1], it was necessary to determine these compounds in very dilute solution (0.001 to 0.25 mg per ml). Since no reducing agent except the polyol was present, a redox procedure seemed appropriate.

The method of REESE AND WILLIAMS[2] failed to give results of sufficient accuracy. The method depends upon the addition of a known quantity of dichromate to the sample and the spectrophotometric determination of the excess dichromate by virtue of its reaction with diphenylcarbazide. The instability of this reagent caused some annoyance, but the major errors arose from the fact that quantity of polyol was found as the difference between two larger quantities. The method of CARDONE AND COMPTON[3] involves the same undesirable subtraction process, although the use of diphenylcarbazide is eliminated by measuring directly the absorbance of the excess dichromate. Periodate is not a satisfactory oxidizing agent for the small quantities of reducing agent encountered in this problem and also fails to oxidize nonvicinal polyols.

In order to avoid the subtraction step, it is necessary to measure the product of the redox reaction rather than the excess dichromate. Fortunately, Cr(III) has an absorbance maximum in 50% sulfuric acid at 610 mμ, at which wavelength dichromate has a much smaller absorptivity. A method was therefore developed for the determination of polyols by oxidizing them in 50% sulfuric acid with dichromate and measuring spectrophotometrically the resultant Cr(III). Since the absorptivity of Cr(III) is rather small, it was necessary to use cells with a light path of 10 cm.

EXPERIMENTAL

Apparatus and reagents

Absorbance measurements were made with a Beckman quartz spectrophotometer, Model DU, equipped to receive 10-cm silica cells.

The oxidizing reagent is 0.1*N* sodium dichromate in concentrated sulfuric acid. About 100 g of sodium dichromate dihydrate are dissolved in water and diluted with water to about 100 ml. Five ml of this solution are added to one liter of reagent-grade, concentrated sulfuric acid. Sodium dichromate is precipitated at this point but redissolves on shaking.

Dextrose from the National Bureau of Standards, lot number 4560, was used as a primary standard after being dried for one hour at 100°. Sodium oxalate of primary-standard grade was also dried for one hour at 100°.

Ethylene glycol, 1,2-propylene glycol, and diethylene glycol were obtained from Eastman Kodak. None of them showed any oxidizable impurity in the chromatographic procedure[1]. Their water contents, as determined by Karl Fischer titration were respectively 0.24, 0.07, and 0.12%. The glycerol was Baker's Analytical Reagent. The chromatographic procedure[1] revealed no oxidizable impurity and the water content was 4.3% by Karl Fischer titration. 2,3-Butylene glycol of technical grade was obtained from the Celanese Corporation of America. Chromatographic analysis[1] indicated the presence of 8.5% (based on the reducing capacity) of an oxidizable impurity of undetermined nature.* The Fischer titration indicated 0.12% water.

Procedure

Pipet 25.00 ml of sample solution containing not more than one meq of polyol into a flask containing 25.00 ml of the oxidizing reagent. Grasp both flask and pipet in one hand and swirl them vigorously during the addition. The temperature of the mixture rises to about 130°. Similarly prepare a blank by adding 25.00 ml of water to 25.00 ml of the oxidizing solution. Heat the flasks in a boiling-water bath for 15 minutes. Then cool them, and measure the absorbance *A* of the solution at 610 mμ in a 10-cm cell against the blank as the comparison solution. One blank may serve for several samples that are run at the same time.

RESULTS

With dextrose and sodium oxalate

Five solutions of dextrose of varying concentration and five solutions of sodium oxalate were treated by the foregoing procedure. The results are summarized in the first four columns of Table I.

TABLE I

OXIDATION OF DEXTROSE AND SODIUM OXALATE

No.	*Compound*	*Taken, meq*	*A*	*a*	*Mean a*	σ
1	dextrose	0.6900	1.02	0.1478	0.1488	0.00089
2	,,	0.5175	0.766	0.1480		
3	,,	0.3450	0.513	0.1487		
4	,,	0.1725	0.258	0.1496		
5	,,	0.06275	0.094	0.1498		
6	sodium oxalate	0.5750	0.853	0.1483	0.1487	0.00056
7	,, ,,	0.4312	0.640	0.1484		
8	,, ,,	0.2875	0.429	0.1492		
9	,, ,,	0.1437	0.213	0.1482		
10	,, ,,	0.0522	0.078	0.1494		
	Mean of 10 determinations			0.14874		

With polyols

Each of the five polyols was treated by the same procedure. These results are listed in the first four columns of Table II.

Calculations

The absorptivity *a* was calculated from the absorbances *A* of the oxidized solutions of dextrose and sodium oxalate by equation (1)

$$a = \frac{A}{10\,c} \tag{1}$$

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* Later investigation of this sample revealed that the major constituent was meso-2,3-butylene glycol and that the "impurity" was the racemic-2,3-butylene glycol.

TABLE II

OXIDATION OF POLYOLS

No.	*Compound*	*Taken, mmol**	*A*	*n*	*Mean n*	*σ*
1	ethylene glycol	0.05077	0.751	9.95	10.03	0.062
2	,,	0.03807	0.571	10.09		
3	,,	0.02538	0.380	10.07		
4	,,	0.01269	0.189	10.02		
5	diethylene glycol	0.03629	1.08	20.01	20.06	0.069
6	,,	0.02468	0.734	20.00		
7	,,	0.01241	0.371	20.10		
8	,,	0.00621	0.186	20.14		
9	glycerol	0.04496	0.935	13.99	14.01	0.022
10	,,	0.03371	0.703	14.02		
11	,,	0.01686	0.351	14.00		
12	,,	0.00843	0.176	14.04		
13	1,2-propylene glycol	0.04032	0.667	11.13	11.13	0.100
14	,,	0.03780	0.620	11.03		
15	,,	0.03362	0.550	11.00		
16	,,	0.02520	0.417	11.13		
17	,,	0.01680	0.280	11.21		
18	,,	0.01260	0.211	11.26		
19	2,3-butylene glycol	0.09683	1.57	10.90	10.94	0.092
20	,,	0.07261	1.18	10.93		
21	,,	0.03632	0.592	10.96		
22	,,	0.01816	0.294	10.89		
23	,,	0.00908	0.150	11.11		
24	,,	0.00454	0.073	10.81		
25	,,	0.00227	0.037	10.96		

* Corrected for water impurity.

where c is the concentration of the reducing agent in milliequivalents per total volume of the mixed solution (sample solution plus oxidizing solution). This volume was constant throughout the experiments at an undetermined value in the vicinity of 50.00 ml. The factor, 10, in the denominator represents the length of the cell. Dextrose has 24 meq per mmol and sodium oxalate has 2 in accordance with the half-reactions.

$$C_6H_{12}O_6 + 6\,H_2O \rightarrow 6\ CO_2 + 24\,H^+ + 24\ e \tag{2}$$

$$C_2O_4^{-2} \rightarrow 2\ CO_2 + 2\ e \tag{3}$$

These values of absorptivity are given in columns 5 and 6 of Table I.

The reduction capacities n of the polyols in milliequivalents per millimole were calculated by equation (4)

$$n = \frac{A}{10\ ac'} \tag{4}$$

where c' is the concentration of the polyol in millimoles per total volume of the mixed solution. These values are given in columns 5 and 6 of Table II.

DISCUSSION

The constancy of the absorptivity values of Table I indicates that dextrose and sodium oxalate are quantitatively oxidized under the recommended conditions according to half-reactions (2) and (3), also that Beer's law is followed.

The complete oxidation of ethylene glycol, diethylene glycol, and glycerol to carbon dioxide may be represented by the half-reactions (5), (6), and (7), respectively.

$$C_2H_6O_2 + 2\ H_2O \rightarrow 2\ CO_2 + 10\ H^+ + 10\ e \tag{5}$$

$$C_4H_{10}O_3 + 5\ H_2O \rightarrow 4\ CO_2 + 20\ H^+ + 20\ e \tag{6}$$

$$C_3H_8O_3 + 3\ H_2O \rightarrow 3\ CO_2 + 14\ H^+ + 14\ e \tag{7}$$

The values of the calculated reduction capacities of these compounds in Table II check the values expected from the foregoing equations, indicating that quantitative oxidation of these polyols is obtained in the recommended procedure.

Propylene glycol may be oxidized according to half-reaction (8) or (9) with reduction capacities of 16 or 12, respectively.

$$C_3H_8O_2 + 4\ H_2O \rightarrow 3\ CO_2 + 16\ H^+ + 16\ e \tag{8}$$

$$C_3H_8O_2 + 2\ H_2O \rightarrow CH_3COOH + CO_2 + 8\ H^+ + 8\ e \tag{9}$$

The observed value of *n* in Table II is between these values, indicating a nonstoichiometric oxidation. However the empirical value of the reduction capacity, 11.13, is constant within the experimental error and may be used in the analysis of solutions of propylene glycol of unknown concentration. The fact that the reduction capacity found in the recommended procedure is higher than that found by CARDONE AND COMPTON[3], 9.0, is probably due to the higher temperature developed on mixing the reagents in the recommended procedure.

Since the 2,3-butylene glycol used in this investigation contained an unidentified impurity, the value of its reduction capacity in Table II, 10.94, cannot be interpreted with confidence. It is probable, however, that this glycol, because of its methyl groups, undergoes a nonstoichiometric oxidation like propylene glycol, which also contains a methyl group. The constancy of the observed *n* for the impure butylene glycol probably means that both this glycol and its impurity have constant reduction capacities in the recommended procedure.

The absorptivity of 0.1487 found in these experiments does not represent the absorptivity of Cr(III) but is the difference between the absorptivity of Cr(III) and that of the dichromate (expressed also in milliequivalents per total volume) at the same wavelength, 610 mμ.

The absorbance of a blank prepared from a fresh oxidizing solution measured in a 10-cm cell against water is about 0.04. This is due in part to the absorbance of the dichromate and in part to Cr(III) formed by reducing impurities in the water or reagents. Blanks prepared from older oxidizing solutions have larger absorbances, probably because of a slow decomposition of the dichromate. However, the older oxidizing solutions may be used without sacrifice of accuracy because the error is eliminated by the use of a blank as the reference solution. For the same reason, it is not necessary to standardize the oxidizing solution.

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SUMMARY

A rapid and accurate method is described for the determination of small quantities of polyhydroxy compounds by the spectrophotometric measurement of Cr(III) produced by the reduction of dichromate in 50% sulfuric acid. The method is probably applicable also to many other organic reducing agents. Duplicate determinations require only 30 minutes. The maximum standard deviation for any of the six compounds investigated was 0.90% of the polyol content.

RÉSUMÉ

Une méthode rapide et précise est décrite pour le dosage de petites quantités de composés polyhydroxylés, au moyen du dichromate en solution dans l'acide sulfurique à 50%; on dose le Cr(III) formé par spectrophotométrie. Cette méthode peut probablement s'appliquer également à beaucoup d'autres réducteurs organiques. Une double détermination peut s'effectuer en 30 minutes. L'erreur maximum pour chacun des six corps étudiés est de 0.90%.

ZUSAMMENFASSUNG

Man beschreibt eine Methode für die Bestimmung von kleinen Mengen von Polyoxyverbindungen durch die spektrophotometrische Messung des Cr(III), das bei der Reduktion des Dichromats in 50% iger Schwefelsäure entsteht. Die Methode ist wahrscheinlich auch für die Bestimmung von vielen anderen organischen Reduktionsmitteln anwendbar. Zweifache Bestimmungen dauern nur 30 Minuten. Der maximale Wert der Standardabweichung ist für jede der sechs untersuchten Verbindungen 0.90% des Gehaltes an Polyoxyverbindung.

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AMPEROMETRIC TITRATION OF MOLYBDENUM

by

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The need for a rapid and precise method for the determination of molybdenum in co-ordination compounds prompted the present investigation. The gravimetric lead molybdate method is too time consuming and a sample containing at least 10 mg of molybdenum is necessary to give the required accuracy. The lead titration procedure requires an external indicator and does not yield satisfactorily precise results.

This method of determining molybdates by precipitation with lead ions suggested the possibility of using lead nitrate solution as a reagent for the amperometric titration of molybdenum. THANHEISER AND WILLEMS[1] have determined molybdenum amperometrically by this method. The precipitation was carried out at 80° C from a potassium nitrate-sodium formate supporting electrolyte which also contained 15% ethanol. These authors used a mercury anode and worked at an applied e.m.f. of 0.6 V. At this voltage only the lead ions were reduced. The end-point was determined from the point where the current suddenly increased due to the addition of excess lead ions. KOLTHOFF AND LINGANE[2] have pointed out the disadvantages of not using the graphical method to determine this end-point. Furthermore, precipitating at this high temperature would require precise temperature control and special precautions to prevent loss of solvent by evaporation.

From the figures reported, the accuracy appears to be of the order of a few percent.

Several methods for the polarographic determination of molybdenum have been described. However, most of the supporting electrolytes used in these methods are not suitable solutions from which to precipitate lead molybdate. They either contain anions which form insoluble precipitates with lead ions[3,4,5,6,7] or which form molybdenum complexes from which lead molybdate cannot be precipitated[8,9,10].

D. F. BOLTZ *et al.*[6] used an acetic acid, acid sodium acetate buffer of pH = 3.5 to examine the polarographic reduction of molybdiphosphoric acid. Since this buffer closely resembles the conditions recommended for the quantitative precipitation of lead molybdate, the behaviour of molybdate ions in this supporting electrolyte was examined.

EXPERIMENTAL

Chemicals. Reagent grade ammonium molybdate was used. The molybdenum content was checked by the gravimetric lead molybdate method and found to contain 54.63 % Mo. All other chemicals used were of reagent grade purity.

Apparatus. The current voltage curves in this research were obtained on a Tinsley chart recording polarograph. The reference electrode was a saturated calomel electrode which was connected to the electrolysis cell through a potassium chloride-agar bridge. The titrations were carried out in a jar using a manual polarograph of the type described by LINGANE AND KOLTHOFF[11]. The galvanometer scale was divided into 100 divisions with full scale deflections of 2, 5, 10 and 20 μA. The jar was fitted with a five-holed stopper to accommodate the dropping mercury electrode, the salt-bridge, the burette and two nitrogen inlets. The hole through which the dropping mercury electrode passed served as the nitrogen outlet. A burette of 5 ml capacity, graduated to 0.01 ml was used.

Polarographic behaviour of molybdenum(VI) in acetic acid buffer

Polarograms were run on $0.6 \cdot 10^{-3}$ M Mo solution in a supporting electrolyte 0.1 M with respect to sodium acetate and potassium chloride and 1.0 M with respect to acetic acid. Molybdenum (VI) is reduced at the dropping mercury electrode in this solution producing a double wave with half-wave potentials at about −0.24 and −0.54 V *vs.* S.C.E. Both waves are irreversible. The height of the second wave appears to be approximately twice that of the first wave (Figure 1). It was not possible to measure these waves accurately for no well-defined plateaux are formed.

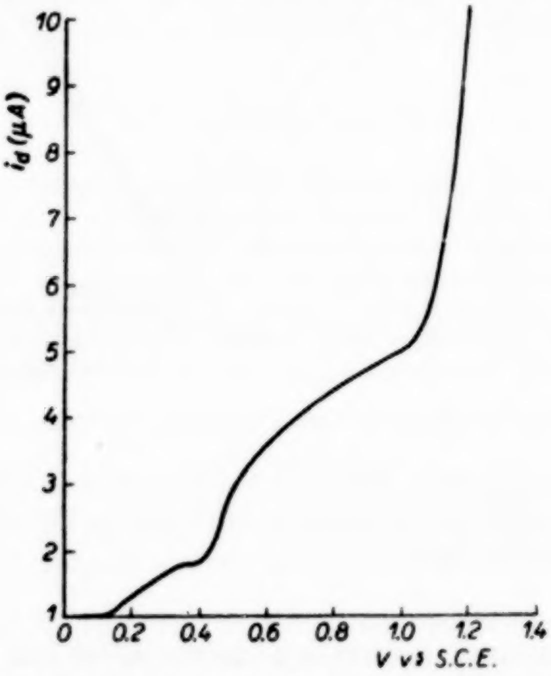

Fig. 1. Typical polarogram for reduction of Mo(VI) in supporting electrolyte 0.1 M CH_3COONa, 0.1 M KCl; 1.0 M CH_3COOH

The investigation of these reduction curves was restricted to an examination of their application to amperometric titrations. The second step had a constant slope between −0.64 and −0.94 V *vs.* S.C.E. It appeared likely that this portion of the curve could be used to produce a diffusion current suitable for amperometric titration.

This was tested by carrying out a titration with lead nitrate and running a complete polarogram after each addition of titre. Excess lead ions produced a well defined reduction wave at −0.45 V *vs.* S.C.E. From the recorded polarograms, graphs were drawn for potentials of −0.6, 0.7, 0.8, 0.9 and 1.0 V. The graphs (Fig. 2) show that the equivalence points obtained at 0.7, 0.8, and 0.9 V coincide with one another and with the theoretical. The end-point at −0.6 V occurs before the equivalence point while the end-point at −1.0 V occurs after the equivalence point. On the basis of these results −0.8 V *vs.* S.C.E. was chosen as the control potential for the titration.

Procedure for amperometric titration of molybdenum

25 ml of the solution containing 0.3 to 3.0 mg of Mo as molybdate are pipetted into 25 ml of the supporting electrolyte of double strength contained in the titration vessel. Oxygen is removed from the solution by passing nitrogen for 10 minutes. A standard solution of lead nitrate (containing 4.25 g $Pb(NO_3)_2$/l) is then added in small increments. The volume of each addition depends on the total molybdenum content of the solution. Nitrogen is then bubbled through the solution for one minute. The pressure of the nitrogen is carefully adjusted at the beginning to cause a bubble to break over the tip of the burette to remove the last drop. The diffusion current is read at a potential of −0.8 V *vs.* S.C.E. one minute after diverting the gas over the

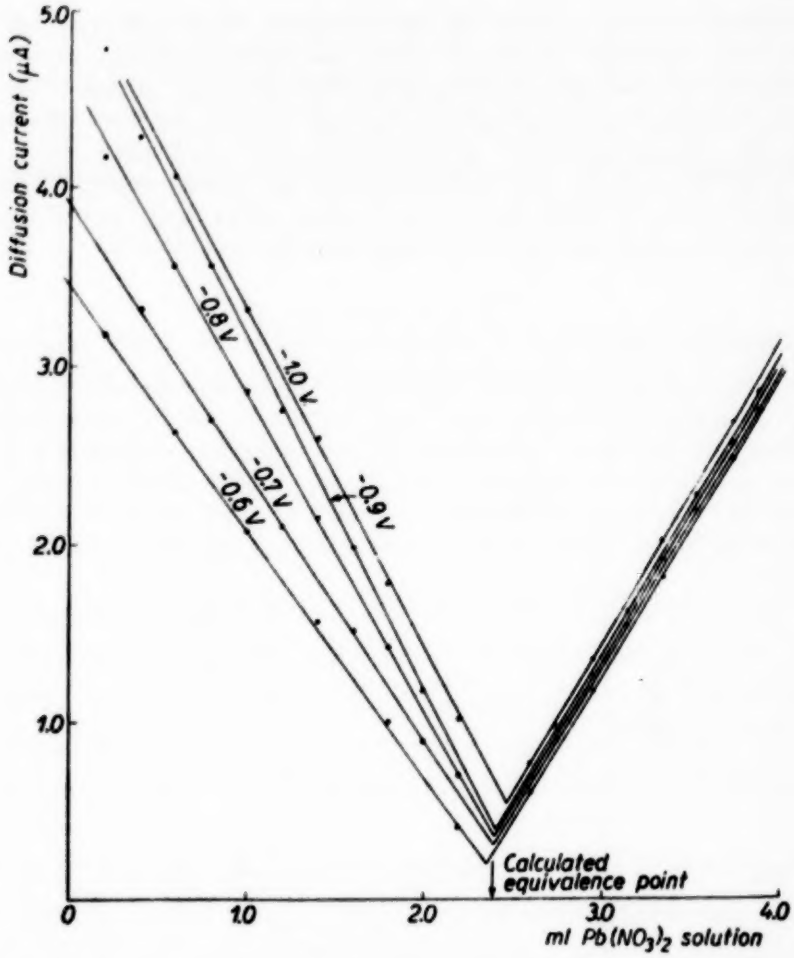

Fig. 2. Amperometric titration of Mo(VI) with $Pb(NO_3)_2$ solution at different control potentials

top of the solution. The readings thus obtained are plotted against ml of titre after correcting for the volume added. The equivalence point is obtained in the usual manner from the point where the two straight lines intersect.

Results

AMPEROMETRIC TITRATION OF MOLYBDENUM(VI) (mg MOLYBDENUM)

Taken	*Found*	*Deviation*	*% error*
2.980	2.998	+0.018	0.6
2.980	2.991	+0.011	0.4
2.980	3.003	+0.023	0.8
1.192	1.189	−0.003	0.25
1.192	1.193	+0.001	0.1
0.596	0.604	+0.008	1.3
0.596	0.599	+0.003	0.5
0.298	0.297	−0.001	0.3
0.298	0.297	−0.001	0.3
		Average	0.4

The analytical precision, over the range tested, is about 0.4%. The lower limit of the method is 0.2 mg Mo in 50 ml of solution ($4 \cdot 10^{-5} M$). In more dilute solutions than this the addition of lead ions increases the diffusion current.

The method is readily applicable to the estimation of molybdenum in co-ordination compounds. The organic matter is destroyed with nitric acid and the solution evaporated to dryness. The residue is dissolved and the molybdate is titrated as described above. The estimation can be completed within thirty minutes. Phosphates, chromates, arsenates and sulphates interfere.

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SUMMARY

A method for the amperometric titration of molybdenum(VI) with lead nitrate solution is described. The precipitation is carried out at room temperature from an acid sodium acetate-potassium chloride supporting electrolyte. The diffusion currents are recorded at a potential of -0.8 V *vs.* S.C.E. where both the lead and molybdenum give reduction waves. While the reduction of molybdenum in acetic acid buffer produces no well defined plateau, it gives accurate and reproducible results amperometrically. The analytical precision is about 0.4%.

RÉSUMÉ

Une méthode est décrite pour le dosage ampérométrique du molybdène(VI) au moyen d'une solution de nitrate de plomb. La précipitation est effectuée à la température ordinaire avec, comme électrolyte de base, une solution d'acétate de sodium — chlorure de potassium. Les courants de diffusion sont enregistrés au potentiel de -0.8 V (par rapport à l'électrode de calomel saturée) auquel soit le plomb, soit le molybdène donnent des vagues de réduction. La réduction du molybdène en tampon acétique ne donne pas de palier bien défini, tandis que les résultats obtenus par ampérométrie sont exacts et reproductibles. La précision analytique est d'environ 0.4 %.

ZUSAMMENFASSUNG

Es wird eine Methode zur amperometrischen Bestimmung von Molybdän(VI) mittels einer Bleinitratlösung beschrieben. Die Ausfällung wird bei gewöhnlicher Temperatur mit einer Lösung von Natriumazetat — Kaliumchlorid als Basiselektrolyt ausgeführt. Die Diffusionsströme werden beim Potential -0.8 V (in Bezug auf die gesättigte Kalomelelektrode) aufgenommen, bei welchem entweder das Blei oder das Molybdän Reduktionssprünge geben. Die Reduktion von Molybdän in einem Azetatpuffer gibt keinen gut definierten Sprung, während die durch Amperometrie erhaltenen Resultate exakt und reproduzierbare sind. Die analytische Präzision ist ungefähr 0.4%.

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HALF-WAVE POTENTIALS OF METAL IONS IN ORGANIC HYDROXYACID SUPPORTING ELECTROLYTES. I

by

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INTRODUCTION

Systematic information concerning the polarographic half-wave potentials of metal ions in various supporting electrolytes can be used in many ways. With its help, the practical analyst can often devise greatly simplified procedures for analysing complex solutions. It provides an immediate insight into the redox chemistry of the metal ions, and serves to indicate ways in which unfamiliar oxidation states can be prepared and stabilized. By identifying complexes which are reversibly reduced, it points the way to more detailed studies of the stoichiometry and thermodynamics of their formation.

Studies of this kind have been carried out recently by LINGANE[5], by WEST, DEAN AND BREDA[18], by PŘIBIL and co-workers[14,15,16], by DESESA, HUME, GLAMM AND DEFORD[2], and by MEITES AND MEITES[12]. The data presented in this paper were secured during the course of an investigation of the effect of the structure of an organic hydroxyacid on its ability to coordinate metal ions.

EXPERIMENTAL

The data in Table V were secured at the Louisiana State University with a photographically recording polarograph (E. H. Sargent and Co., Model XI) equipped with a d'Arsonval galvanometer. Some polarograms were obtained with a Heyrovsky-type cell, using a microcalomel reference electrode[17] as the anode; others were obtained with a conventional H-cell[6]. The concentration of the metal ion was varied from 0.01 to 10 mM, and the malonate concentration from 0.25 to 0.50M, while the concentration of gelatin was kept constant at 0.01%.

The remaining data were secured at Yale University with a pen-and-ink recording polarograph[10] whose initial and span e.m.f. voltmeters had been carefully calibrated with a Rubicon precision potentiometer. The measured half-wave potentials were corrected for the iR drops through both the polarograph and the modified H-cell[11] used. The operation of the apparatus was checked by frequently recording polarograms of cadmium(II) in 0.10M potassium nitrate. When the corrected value of $E_{1/2}$ differed by more than two or three millivolts from the literature value[1,4,7], the saturated calomel electrode and saturated potassium chloride agar bridge were replaced.

In these experiments the concentration of metal ion was always very nearly 1.0 mM, excepting that of thallous ion, which was always 0.2 mM. Unless otherwise noted in the Tables, no maximum suppressor was added.

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Reagent grade chemicals were used for the preparation of all solutions in both laboratories. The stock metal ion solutions employed at the Louisiana State University for the measurement of diffusion current constants were standardized by gravimetric or electrogravimetric methods. All solutions were deaerated with tank nitrogen or hydrogen, and Beckman Model G pH meters were used for all pH measurements. The drop times were always between 2.5 and 6 seconds.

The following symbols are used in the Tables. ">O" denotes a wave which begins at a potential so positive that it merges with the anodic wave due to dissolution of the electrode mercury, and carries no implication as to whether $E_{1/2}$ would actually be positive or negative if it could be measured. A value of $E_{1/2}$ enclosed in parentheses denotes an anodic wave. "NR" signifies that no wave is obtained. "w.-d." and "i.-d." mean well- and ill-defined, respectively, the criterion being the degree of accuracy with which, in our opinion, the height of the wave could be measured. A wave described as "very w.-d.", for example, is suited for the precise polarographic determination of the substance responsible for it; a "very i.-d." wave, on the other hand, merely serves to interfere with other waves, and is useless for any quantitative purpose whatever. Descriptions intermediate between these are necessarily matters of personal judgment.

The interpretation of these and other similar data derived from continuing work will be deferred until a later paper in this series.

TABLE I

HALF-WAVE POTENTIALS IN SATURATED CITRIC ACID

Element and oxidation state	$E_{1/2}$ *vs. S.C.E. volts*	*Formula or oxidation state of product*	*Notes*
Ag(I)	>0	0	Rounded max., very w.-d.
As(III)	−0.58	0(film?(3,9))	Very i.-d.
	−0.73	0	I.-d.
	−1.02	−III	I.-d., max. not suppressed by 0.002% Triton X-100
As(V)	NR		
Bi(III)	−0.025	0	W.-d., slightly irreversible
Cd(II)	−0.514	0	Very w.-d., reversible
Ce(III)	NR		
Ce(IV)	—		Rapidly reduced to Ce(III), *q.v.*
Co(II)	NR		
Cr(III)	−0.78	II	I.-d., reversible
Cr(VI)	>0	III	Large rounded max., w.-d., no indication of wave at −0.78 V
Cu(II)	+0.03	0	Small max., very w.-d., slightly irreversible
Fe(II)	NR		
Fe(III)	+0.23	II	W.-d., reversible
In(III)	-0.54_0	0	W.-d., irreversible
Mn(II)	NR		
Mo(VI)	+0.038	V	Very w.-d., reversible
	-0.43_7	III	Very w.-d., irreversible
Ni(II)	−0.98	0	I.-d., irreversible
Pb(II)	−0.358	0	W.-d., reversible
Sb(III)	-0.37_6	0	Very w.-d., irreversible
Sb(V)	NR		
Sn(II)	(−0.05)	IV	Fairly w.-d., reversible
	−0.40	0	Very w.-d., reversible
Sn(IV)	NR		
Te(VI)	NR		
Tl(I)	−0.442	0	Very w.-d., reversible
U(VI)	−0.122	IV(?)	Very w.-d.; $E_{3/4}$-$E_{1/4}$ = −63 mV
V(IV)	−0.67	?	Small i.-d. pre-wave
	−1.05	II	I.-d., irreversible
V(V)	$+0.10_8$	IV	Very w.-d., reversible
	−0.63	II	Fairly i.-d., irreversible
W(VI)	NR		
Zn(II)	−0.930	0	Fairly i.-d., reversible

TABLE II

HALF-WAVE POTENTIALS IN SATURATED MALONIC ACID

Element and oxidation state	*$E_{1/2}$ vs. S.C.E. volts*	*Formula or oxidation state of product*	*Notes*
As(III)	−0.70	0(?)	Fairly i.-d., irreversible; may actually be poorly resolved double wave
As(V)	NR		
Bi(III)	+0.010	0	Large max. nearly unaffected by 0.002% Triton X-100, very w.-d.
Cd(II)	−0.519	0	Reversible, very w.-d.
Ce(III)	NR		
Ce(IV)	—		Rapidly reduced to Ce(III), *q.v.*
Co(II)	NR		
Cr(III)	-0.8_5	II(?)	Very small, very i.-d.
Cr(VI)	>0	III	Huge max., very w.-d.; height is only about 2/3 the predicted value for $n = 3$
Cu(II)	+0.081	0	Very w.-d., slightly irreversible
Fe(II)	NR		
Fe(III)	>0	II	Very w.-d.
Fe(III)[a]	+0.202	II	Very w.-d., reversible
In(III)	−0.504		Very i.-d.
	−0.61	0	Plateau has abnormally large positive slope. Waves are due to two species in sluggish equilibrium.
Mn(II)	NR		
Mo(VI)	+0.073	V	Very w.-d., irreversible
	−0.228	III	Very w.-d., slightly irreversible
Ni(II)	−0.97	0	I.-d., irreversible
Pb(II)	NR		Complete pptn.; $E_{1/2} = -0.375$ V for very w.-d. reversible wave in half-saturated malonic acid
Sb(III)	−0.118	0	Very w.-d., nearly reversible
Sb(V)	NR		
Sn(II)	(+0.015)	IV	Fairly w.-d., nearly reversible
	−0.397	0	Very w.-d., reversible
Sn(IV)	NR		
Te(VI)	NR(?)		Final current rise starts abnormally early, at −0.95 V
Tl(I)	−0.440	0	Reversible
U(VI)	−0.12	IV	Very w.-d.; $E_{3/4}-E_{1/4} = -57$ mV
	−1.1(?)		Some indication of an i.-d. irreversible wave
V(IV)	−0.64		Pre-wave
	−1.08	II	Very i.-d., very irreversible
V(V)	>0	IV	Fairly w.-d.
	−0.67	II(?)	
W(VI)	NR(?)		Final current rise starts at −0.8 V, but no plateau is found: catalytic reduction of H+?
Zn(II)	-0.9_4	0	Very i.-d.

[a]: with 0.002% Triton X-100

TABLE III

HALF-WAVE POTENTIALS IN SATURATED TARTARIC ACID

Element and oxidation state	*$E_{1/2}$ vs. S.C.E. volts*	*Formula or oxidation state of product*	*Notes*
Ag(I)	>0	0	Small rounded max., w.-d.
As(III)	−0.37		Fairly w.-d.
	−0.45		Rounded max., i.-d.
	—0.62	−III	Fairly w.-d.

TABLE III (continued

Element and oxidation state	*$E_{1/2}$ vs. S.C.E. volts*	*Formula or oxidation state of product*	*Notes*
As(V)	−1.0		Very i.-d.
Bi(III)	-0.06_0	0	W.-d., slightly irreversible
Cd(II)	−0.564	0	Very w.-d., reversible
Ce(IV)	+0.25	III	
Co(II)	NR		
Cr(III)	−0.91	II	Very i.-d., irreversible
Cr(VI)	—		Rapidly reduced to Cr(III), *q.v.*
Cu(II)	>0		I.-d.
	−0.08		I.-d.
	−0.34		Very w.-d.
Fe(II)	NR		
Fe(III)	>0	II	W.-d.
In(III)	−0.527	0	Reversible; plateau has abnormally large positive slope
Mn(II)	NR		
Mo(VI)	-0.08_4	V	Fairly w.-d., irreversible
	−0.391	III	Very w.-d., irreversible
Ni(II)	−1.05	0	Fairly i.-d.
Pb(II)	−0.40	0	Very w.-d., reversible
Sb(III)	−0.41	0	Very w.-d., slightly irreversible
Sb(V)	NR		
Sn(II)	(−0.08)	IV	W.-d., reversible
	−0.44	0	Very w.-d., reversible
Sn(IV)	NR		
Te(VI)	−0.83	?	Abnormally small
Tl(I)	−0.473	0	Very w.-d., reversible
U(VI)	-0.11_5	IV(?)	W.-d., rounded max.; $E_{3/4}$-$E_{1/4}$ = −51 mV
V(IV)	+0.03		Two small i.-d. irreversible waves
	−0.40		
	−0.75	II	I.-d., very irreversible
V(V)	+0.25	IV	Fairly w.-d.
	−0.75	II	I.-d., very irreversible
W(VI)	−0.9		Some indication of a very irreversible wave; *cf.* Table II
Zn(II)	−1.03	0	Fairly w.-d.

TABLE IV

HALF-WAVE POTENTIALS IN 0.5*M* SODIUM HYDROGEN MALONATE — 0.5*M* DISODIUM MALONATE, pH 4.8

Element and oxidation state	*$E_{1/2}$ vs. S.C.E. volts*	*Formula or oxidation state of product*	*Notes*
As(III)	−1.00	?	Very i.-d.
As(V)	NR		
Bi(III)	−0.195	0	Very w.-d., slightly irreversible
	−1.20		Anomalous[a,8,13]
Cd(II)	−0.648	0	Very w.-d., reversible
	−1.17		Anomalous[a]
Ce(IV)	>0	III	Very w.-d.
	−1.16		Anomalous[a]
Co(II)	NR		
Cr(III)	−1.0	II	Small, i.-d., very irreversible[a]
Cr(VI)	>0	III	Large max., very w.-d.
	−1.16		Anomalous[a]
Cu(II)	−0.170	0	Very w.-d., reversible
	−1.16		Anomalous[a]

TABLE IV (cotinued)

Element and oxidation state	*$E_{1/2}$ vs. S.C.E. volts*	*Formula or oxidation state of product*	*Notes*
Fe(II)	(−0.250)	III	Very w.-d., reversible
Fe(III)	−0.255	II	Very w.-d., reversible
	−1.16		Anomalous[a]
Fe(III)[b]	−0.250	II	Very w.-d., reversible
In(III)	−0.19	?	Both very i.-d. and almost completely eliminated by 0.004% Triton X-100
	−0.72	?	
Mn(II)	NR		
Mo(VI)	−0.67	IV	Fairly i.-d., very irreversible
	−1.21	III	Fairly i.-d., irreversible
Ni(II)	−1.13		I.-d. triple wave[a]
	−1.28		
	−1.50		
Pb(II)	−0.481	0	Very w.-d , reversible
	−1.16		Anomalous[a]
Sb(III)	-0.47_8	0	Small acute max. on rising portion of wave simulates double wave; very w.-d., slightly irreversible
Sb(V)	NR		
Sn(II)	(−0.293)	IV	Very w.-d., reversible
	−0.605	0	Very w.-d., reversible
Sn(IV)	NR		
Te(VI)	−1.17		Fairly i.-d., irreversible
Tl(I)	−0.474	0	Very w.-d., reversible
	−1.16		Anomalous[a]
U(VI)	−0.437	IV	Very w.-d.; $E_{3/4}$-$E_{1/4}$ = −51 mV
	−1.19	III	Very i.-d., very irreversible
V(IV)	−1.34	II	Very i.-d., irreversible
V(V)	>0	IV	Very w.-d.
	−1.33	II	I.-d., irreversible
W(VI)	−1.38	?	Large acute max., i.-d.
W(VI)[b]	−1.39	III(?)	Fairly w.-d.; $E_{3/4}$-$E_{1/4}$ = −46 mV
Zn(II)	-1.14_6	0	Fairly w.-d., reversible

[a]: Eliminated by 0.002% Triton X-100
[b]: With 0.002% Triton X-100

TABLE V

HALF-WAVE POTENTIALS IN 0.5*M* MALONATE — 0.01% GELATIN, pH 0.1-9

Element and oxidation state	*$E_{1/2}$ vs. S.C.E. volts*	*Formula or oxidation state of product*	*Notes*
Ag(I)	>0	0	Rapidly reduced by Hg pool
Al(III)	NR		
Au(III) (AuCl$_4^-$)	NR		
Bi(III)	−0.084	0	pH 2.18, w.-d., irreversible. *I* = 3.72. Unsatisfactory at pH<2
Bi(III)	−0.196	0	pH 4.54, w.-d., irreversible. *I* = 3.72
Bi(III)	−0.248	0	pH 5.69, w.-d., irreversible. *I* = 3.72
Cd(II)	$-0.65_7 \pm 0.01_2$	0	pH 4.6-6, w.-d., reversible. *I* = 2.93. Unsatisfactory at pH<4.5
Co(II)	NR		
Cr(III)	NR		
Cu(II)	−0.006±0.002	0	pH 0.1-1.5, very w.-d., reversible. *I* = 3.55. Unsatisfactory with < 0.1 m*M* Cu(II)

TABLE V (continued)

Element and oxidation state	*$E_{1/2}$ vs. S.C.E. volts*	*Formula or oxidation state of product*	*Notes*
I(V) (IO_3^-)	−0.77	−I	pH$<$4.0, w.-d., irreversible. $I = 9.94$
I(V) (IO_3^-)	−0.77		4.0 $\leq$ pH $\leq$ 6.0. $I_{total} = 9.94$
	−1.14	−I	
I(V) (IO_3^-)	−1.14	−I	pH$>$6.0. $I = 9.94$
Ir(IV)	NR		
Mn(II)	NR		
Ni(II)	NR		
Os(VIII)	NR		
Pb(II)	−0.495 ± 0.002	0	pH 5.7-6.0, 1 m*M* Pb(II), w.-d., reversible. $I = 3.29$
Pt(IV)	NR		
Sb(III)	not satisfactorily measurable		Poorly resolved double wave (second wave begins at *ca.* −0.3 V)
Se(IV)	−0.742	0(?)	pH 5.2-5.8, 1 m*M* Se(IV), fairly w.-d., irreversible. $I = 5.06$
Se(IV)	−0.802	0(?)	pH 5.2-5.8, 5 m*M* Se(IV), fairly w.-d., irreversible
Se(IV)	−0.74	0(?)	pH$>$5.8
	−1.41	?	$E_{1/2}$ independent of Se concn.
Se(VI)			Virtually identical with Se(IV) in every respect
Sn(II)	(−0.265)	IV	
	−0.664	0	
Sn(IV)	NR		
Te(VI)	−1.57	0(?)	pH 5.7-8.7, 0.06 m*M* Te(VI), w.-d., irreversible, $\triangle E_{1/2}/\triangle \log$ [Te(VI)] = −0.060 V
Te(VI	−1.33	0(?)	pH 5.64, 0.06 m*M* Te(VI), w.-d., irreversible, $\triangle E_{1/2}/\triangle \log$ [Te(VI)] = −0.060 V
Te(VI)	−1.30	0(?)	pH 4.95, 0.06 m*M* Te(VI), w.-d., irreversible, $\triangle E_{1/2}/\triangle \log$ [Te(VI)] = −0.060 V
Te(VI)	—		pH 4.07, 0.06 m*M* Te(VI), very i.-d.
Tl(I)	−0.492 ± 0.006	0	pH 2.2-5.6, 0.01 m*M* Tl(I), very w.-d., reversible. $I = 2.46$

TABLE VI

HALF-WAVE POTENTIALS IN 1*M* DISODIUM MALONATE – 0.2*M* SODIUM CARBONATE – 0.2*M* SODIUM BICARBONATE, pH 10.0

Element and oxidation state	*$E_{1/2}$ vs. S.C.E. volts*	*Formula or oxidation state of product*	*Notes*
As(III)	(−0.02)	V	Very i.-d., slightly irreversible
As(V)	NR		
Bi(III)[a]	-0.51_9	0	Very w.-d., slightly irreversible
	−1.29		Anomalous[b]
Cd(II)[a]	−0.692	0	Very w.-d., reversible
	−1.28		Anomalous[b]
Ce(IV)	−0.058	III	W.-d., reversible
	−1.25		Anomalous[c]
Co(II)	−1.59	0	Fairly w.-d., very irreversible
Cr(III)	NR		
Cr(VI)	−0.40	III	I.-d.; shape greatly improved by 0.002% Triton X-100
Cu(II)	−0.220	0	Very w.-d., reversible
	−1.31		Anomalous[b]

TABLE VI (continued)

Element and oxidation state	*$E_{1/2}$ vs. S.C.E. volts*	*Formula or oxidation state of product*	*Notes*
Fe(II)	(−0.512)	III	Very w.-d., reversible
	−1.62	0	Fairly w.-d., irreversible
Fe(III)	−0.518	II	W.-d., reversible
	−1.65	0	I.-d., irreversible
In(III)	−1.32	0	Very w.-d., irreversible, probably includes anomalous wave
In(III)[d]	−1.30	0(?)	Very i.-d., very irreversible
	−1.61		Probably anomalous
Mn(II)	NR		
Mo(VI)	NR		
Ni(II)	−1.14		Very i.-d., irreversible
	−1.36		Fairly i.-d., irreversible
Pb(II)[a]	−0.616	0	Very w.-d., reversible
	−1.28		Anomalous[c]
Sb(III)	(-0.12_2)	V	W.-d., irreversible
	−0.864	0	W.-d., nearly reversible
Sb(V)	-0.1_4		Four very small, fairly w.-d., irreversible waves
	-0.4_6		
	-0.8_8		
	-1.2_6		
Sn(II)	(−0.638)	IV	Very w.-d., irreversible
	−0.817	0	Very w.-d., reversible
	−1.28		Anomalous
Sn(IV)	−1.25	0(?)	I.-d., very irreversible
Sn(IV)[d]	−1.22	II(?)	Very i.-d., irreversible
	−1.64	0(?)	Probably not anomalous; total wave height is unaffected by Triton
Te(VI)	−1.38	?	Fairly i.-d.
Tl(I)	−0.483	0	Very w.-d., reversible
	−1.30		Anomalous[b]
U(VI)	−0.90	V	Fairly i.-d., irreversible
	−1.29		Anomalous[b]
V(IV)	(−0.380)	V	Very w.-d., slightly irreversible
	−1.17		Very irreversible pre-wave
	−1.59	II	Fairly i.-d., irreversible
V(V)	−1.18	IV	Very i.-d., irreversible
	−1.59	II	Fairly w.-d., irreversible
W(VI)	NR		
Zn(II)	-1.28_5	0	W.-d., irreversible

[a]: Extensive precipitation from a 1 m*M* solution
[b]: Shifted to −1.62 ± 0.02 V and considerably decreased in height by 0.002% Triton X-100
[c]: Eliminated by 0.002% Triton X-100
[d]: With 0.002% Triton X-100

TABLE VII

HALF-WAVE POTENTIALS IN 1 *M* DISODIUM MALONATE — 1 *M* SODIUM HYDROXIDE

Element and oxidation state	*$E_{1/2}$ vs. S.C.E. volts*	*Formula or oxidation state of product*	*Notes*	
As(III)	(−0.273)	V	W.-d., reversible	
As(V)	-1.1_4		Very small, i.-d.	
Bi(III)	-0.68_6	0	W.-d., slightly irreversible	
	−1.23		Anomalous	
Cd(II)[a]	−0.94		Decreases on standing	all i.-d.
	−1.20		Probably anomalous	
	−1.55		Increases on standing	

TABLE VII (continued)

Element and oxidation state	*$E_{1/2}$ vs. S.C.E. volts*	*Formula or oxidation state of product*	*Notes*
Cd(II)[a,b]	−0.86		Very small, i.-d., irreversible
	−1.59		I.-d., probably anomalous
Ce(III)[a]	NR		
Ce(IV)	—		Rapidly reduced to Ce(III), *q.v.*
Co(II)	−1.52	0	Small, very i.-d., irreversible
Cr(III)	−0.92	II	Small, w.-d., reversible
Cr(VI)	−0.75	III	Fairly w.-d., irreversible
	−1.16		Probably anomalous
Cr(VI)[b]	-0.77_0	III	W.-d., irreversible
Cu(II)	-0.35_7		Very i.-d. } both reversible; two complexes
	-0.44_7	0	Very w.-d. } in sluggish equilibrium
	−1.26		Anomalous
Cu(II)[b]	-0.36_6		I.-d. } *vide supra*
	-0.44_8	0	Very w.-d. }
	−1.55		Anomalous
Fe(II)[a]	(−0.96)	III	
	−1.56	0	Very small; fairly w.-d.
Fe(III)	−0.90	II	Fairly i.-d., irreversible
	−1.19		Anomalous
	−1.57	0	Fairly i.-d., slightly irreversible
Fe(III)[b]	−0.89	II	Fairly w.-d., irreversible
	−1.61	0	I.-d., irreversible, includes anomalous wave
In(III)	−1.12	0(?)	W.-d., irreversible, includes anomalous wave
Mn(II)[a]	(−0.43)	III(?)	Very small, i.-d., irreversible
	−1.72	0	Very i.-d., slightly irreversible
Mo(VI)	−0.90	?	Very small, irreversible
Ni(II)	NR		
Pb(II)	−0.754	0	Very w.-d., reversible
	−1.29		Anomalous
Pb(II)[b]	−0.757	0	Very w.-d., reversible
Sb(III)	(-0.47_5)	V	Very w.-d., slightly irreversible
	-1.13_7	0	Fairly i.-d., irreversible
	−1.41		Possibly anomalous
Sb(V)	NR		
Sn(II)	(-0.95_2)	IV	Large acute max., very w.-d.
	-1.13_7	0	Large acute max., i.-d
	−1.39		Anomalous
Sn(II)[b]	(−0.934)	IV	Very w.-d., slightly irreversible
	-1.14_8	0	W.-d., slightly irreversible
	−1.60		Anomalous
Sn(IV)	NR		
Te(VI)	−1.52		Fairly i.-d., irreversible
Tl(I)	−0.477	0	Very w.-d., reversible
	−1.29		Anomalous
U(VI)	−0.908	V(?)	Fairly w.-d., reversible (?)
	−1.24		} Two i.-d. very irreversible waves of approximately equal heights
	−1.63		}
U(VI)[b]	−0.906	V(?)	Very w.-d., reversible (?)
	−1.60	IV(?)	I.-d., very irreversible
V(IV)	(-0.44_0)	V	Very w.-d., irreversible
	−1.68	II	Very i.-d., irreversible
V(V)	-1.67_4	II	Very i.-d., irreversible
W(VI)	−0.90	?	Small, fairly w.-d.
	−1.22		Probably anomalous
W(VI)[b]	−0.90	?	Small, w.-d.
Zn(II)	−1.482	0	Very w.-d., irreversible

[a]: Extensive precipitation from a 1 m*M* solution
[b]: With 0.002% Triton X-100

TABLE VIII

HALF-WAVE POTENTIALS IN 1*M* SODIUM LACTATE — 1*M* SODIUM HYDROXIDE

Element and oxidation state	$E_{1/2}$ *vs. S.C.E. volts*	*Formula or oxidation state of product*	*Notes*
Ag(I)[a]	>0	0	
As(III)	(−0.27)	V	Fairly w.-d., nearly reversible
As(V)	NR		
Bi(III)	-0.71_5	0	Fairly i.-d., slightly irreversible
	−1.10		Anomalous
Cd(II)	−0.83	0	Small, fairly w.-d.
	−1.12		Anomalous
Ce(III)	NR		
Ce(IV)	—		Rapidly reduced to Ce(III), *q.v.*
Co(II)	−1.62	0	Very i.-d., irreversible
Cr(III)	NR		
Cr(VI)	−0.80	III	Very w.-d.
Cu(II)	-0.51_5	0	W.-d., slightly irreversible
	−1.13		Anomalous
Fe(II)	(−0.98)	III	W.-d., reversible
	−1.66	0	Fairly w.-d., slightly irreversible
Fe(III)	−1.00	II	Irreversible
	−1.67	0	Slightly irreversible
Mn(II)	(−0.46)	III(?)	Abnormally small, irreversible
	−1.76	0	Fairly w.-d., nearly reversible
Mo(VI)	NR		
Ni(II)[a]	NR		
Pb(II)	−0.772	0	I.-d., reversible
	−1.11		Anomalous
Pb(II)[b]	−0.771	0	Very w.-d., reversible
	−1.41		Anomalous
Sb(III)	(−0.46)	V	Very w.-d., slightly irreversible
	−1.17	0	W.-d., irreversible
Sb(V)	NR		
Sn(II)	(−0.95)	IV	Very w.-d., nearly reversible
	−1.15	0	Very w.-d., nearly reversible, includes anomalous wave ($i_c > i_a$)
Sn(IV)	>0		Three small waves of approximately equal heights. No waves observed with 5 m*M* Sn(IV)
	−1.09		
	−1.48		
Sn(IV)[b]	>0		Very small
	−1.6		I.-d., very irreversible. Total wave height is greatly decreased by Triton
Te(VI)	−1.54	0(?)	Fairly w.-d., irreversible
Tl(I)	−0.485	0	Fairly w.-d., reversible
	−1.09		Two very irreversible waves
	−1.34		
Tl(I)[b]	−0.485	0	Very w.-d., reversible
	−1.40		Fairly w.-d., irreversible
	−1.66		
U(VI)	−0.95	V(?)	I.-d.
	−1.7	IV(?)	Very i.-d.
U(VI)[b]	−0.93	V	Fairly w.-d., reversible
	−1.67	IV(?)	Fairly i.-d., irreversible
V(IV)	(−0.51)	V	W.-d., reversible
	−1.70	II	Very i.-d., irreversible
V(V)	−1.71	II(?)	Very i.-d., very irreversible
W(VI)	−1.1	?	Abnormally small, irreversible, eliminated by 0.002% Triton X-100
Zn(II)	−1.50	0	W.-d., slightly irreversible

[a]: Extensive precipitation from a 1 m*M* solution
[b]: With 0.002% Triton X-100

SUMMARY

Eight new media containing organic hydroxyacids and their anions have been investigated as supporting electrolytes for polarographic analysis. For over 25 metal ions in each of these media there are tabulated the half-wave potentials, reversibilities and probable products of the electrode reactions, descriptions of the wave forms, and other data of polarographic importance.

RÉSUMÉ

Huit nouveaux milieux, renfermant des hydroxyacides et leurs sels, ont été étudiés comme électrolytes de base dans l'analyse polarographique, pour plus de 25 cations. Les potentiels de demi-onde, les réversibilités et les produits de réaction aux électrodes, les descriptions des formes des ondes et d'autres renseignements polarographiques sont donnés dans des tableaux.

ZUSAMMENFASSUNG

Es wurden acht neue Medien, welche Hydroxysäuren und ihre Salze enthalten, als Basiselektrolyte in polarographischen Analysen für mehr als 25 Kationen untersucht. Die Halbwertspotentiale, die Reversibilität und die Reaktionsprodukte an den Elektroden, die Beschreibung der Form der Wellen und andere polarographische Einzelheiten werden in Tabellen angegeben.

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BUCHBESPRECHUNG

Leichtmetallanalyse, von H. Ginsberg, 3. Auflage, Verlag Walter de Gruyter u. Co., Berlin 1955, XIX + 285 Seiten, 79 Abb., Ganzleinen 24,80 DM.

Die nunmehr vorliegende 3. Auflage dieses Buches unterscheidet sich wesentlich von den früheren Auflagen. Gliederung und Anordnung des Stoffes ist vollständig umgestaltet und auch der Inhalt ist in Vielem abgeändert worden, um den Fortschritten der analytischen Arbeitsmethodik seit der letzten Auflage Rechnung zu tragen.

In einem allgemeinen Teil wird zunächst die Probenahme und die Vorbereitung der Proben für die chemische Analyse getrennt für Aluminium verschiedenen Reinheitsgrades, Beryllium, Magnesium und Titan, sowie die Probenahme und Vorbereitung der Proben für die Spektralanalyse besprochen. Der Referent würde es allerdings begrüßen, wenn wegen der grundlegenden Bedeutung der Probenahme für jede analytische Untersuchung, die Ausführungen zu diesem Punkte etwas umfangreicher wären und mehr in's Einzelne gingen. Ferner wird eine Zusammenstellung der verschiedenen Möglichkeiten zum Auflösen von metallischem Aluminium, Beryllium, Magnesium und Titan gegeben und schließlich werden in einem „Meßmethoden und Meßgeräte" überschriebenen Kapitel einige allgemein gehaltene Bemerkungen über Gewichtsanalyse, Maßanalyse, elektrolytische Verfahren, Polarographie, Kolorimetrie und Photometrie, Flammenphotometrie und Spektrographie gemacht.

In den dann folgenden speziellen Teilen wird die Analyse der Metalle Aluminium (153 Seiten), Beryllium (12 Seiten), Magnesium (25 Seiten), Titan (32 Seiten) und ihrer Legierungen behandelt. Auch einige orientierende Kurzmethoden, die dazu dienen können, die Legierungsgattung zu bestimmen, zu der das Material eines beliebigen Werkstückes zu zählen ist, sind angegeben. Im Interesse der Schnelligkeit bei der Analysendurchführung zieht man es heute im Allgemeinen vor, die einzelnen Elemente unter Verwendung gesonderter Einwagen und spezieller Verfahren in Einzelbestimmungen zu ermitteln. Der Verfasser hat deshalb die in den früheren Auflagen gebrachten Trennungsgänge fortfallen lassen und gibt dafür Arbeitsvorschriften zur Bestimmung jeweils nur eines Bestandteiles für ein bestimmtes vorliegendes Probematerial. Diese Arbeitsvorschriften sind aber so gestaltet, daß es für den Erfahrenen leicht ist, sich im Bedarfsfalle einen geeigneten Trennungsgang zusammenzustellen.

Die in früheren Auflagen benutzte Anordnung des Stoffes nach den Arbeitsweisen ist zugunsten einer alphabetischen Ordnung nach den zu bestimmenden Elementen aufgegeben worden. Es muß dies als eine wesentliche Verbesserung bezüglich der Übersichtlichkeit und der Bequemlichkeit bei der praktischen Verwendung des Buches bezeichnet werden.

Bei der Besprechung der zur Bestimmung der einzelnen Bestandteile vorgeschlagenen Verfahren werden zunächst deren Grundlagen, Anwendungsbereich, Genauigkeit und Störungen kurz beschrieben und besondere Hinweise für ihre Durchführung gegeben; es folgt dann eine Zusammenstellung der erforderlichen Reagenzien und eine Arbeitsvorschrift. Hervorzuheben ist die übersichtliche Darstellung des Gebotenen, die in straffer Zusammenfassung nur das Wesentliche, aber dieses mit einer für den erstrebten Zweck völlig genügenden Ausführlichkeit bringt. Häufig werden zur Bestimmung eines Elementes mehrere verschiedene Wege angegeben. Bei photometrischen Verfahren sind durchweg die Extinktionskurven der zu messenden gefärbten Lösungen abgebildet.

Von einer Bevorzugung einer bestimmten Gruppe von Verfahren bei den zur Bestimmung der verschiedenen Elemente gegebenen Arbeitsvorschriften kann keine Rede sein. So finden sich neben Methoden, die seit Jahrzehnten bekannt und bewährt sind Verfahren, die erst in allerletzter Zeit entwickelt wurden; neben rein chemischen werden auch physikalische Verfahren vorgeschlagen. Daß die polarographischen und besonders die photometrischen Verfahren gegenüber den früheren Auflagen hier einen breiteren Raum einnehmen, ist eine Folge der immer weiter gesteigerten Reinheit technisch dargestellter Metalle, wodurch auch im Rahmen von Routine-Analysen die Durchführung von Spurenbestimmungen erforderlich wird. Dies ist bei der Auswahl der beschriebenen Analysenverfahren berücksichtigt worden.

Es liegt in der Natur eines Buches, das von einem Praktiker für die Praxis geschrieben wurde, daß eine Vollständigkeit bei der Darstellung der verschiedenen Möglichkeiten nicht angestrebt wird, sondern daß aus der Fülle der bekannten Verfahren diejenigen herausgestellt werden, die zuverlässig, schnell, wenig störanfällig und einfach durchzuführen sind und die sich im Laufe einer längeren Laboratoriumspraxis als für einen bestimmten Fall besonders geeignet erwiesen haben. Diese Auswahl ist dem Verfasser vorzüglich gelungen. Man darf deshalb die vorliegende 3. Auflage der „Leichtmetallanalyse" wohl als eine Standardsammlung der bei der Untersuchung entsprechender Materialien anzuwendenden Analysenverfahren bezeichnen. Sie dürfte z.Z. auf keine normalerweise bei der Analyse von Leichtmetallen gestellte Frage die Antwort schuldig bleiben und wird deshalb jedem, der auf diesem Gebiet zu arbeiten hat, schon nach kurzem Gebrauche unentbehrlich werden.

H. Bode (Hannover)

ON THE REACTIVITY OF BENZIDINESULFONIC ACIDS AND THEIR APPLICATIONS IN ANALYSIS

REACTION OF CUPRIC SALTS WITH *O*-BENZIDINEMONOSULFONIC ACID IN PRESENCE OF ALKALI THIOCYANATE

by

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Part of our research work on the reactivity of benzidinedisulfonic acids has already been published[1,2,3]. We study in the present paper the reaction which takes place when first ammonium thiocyanate and then a solution of the ammonium salt of *o*-benzidinemonosulfonic acid are added to a cupric salt.

Under such conditions we do not observe the red precipitate described in one of the papers mentioned above and given by cupric salts with the same acid when thiocyanates are not present, but another one, blue, and flaky when the copper concentration is sufficiently high. At lower concentrations there is only a blue coloring.

In order to obtain this precipitate or coloring, it is necessary — as in all reactions given by cupric salts with other amines, thiocyanates being present — that the initial concentrations of Cu^{II} should be low enough to avoid the precipitate of cupric thiocyanate; in this case, a slight excess of SCN^- is also necessary, otherwise the red precipitate already described and which appears in solutions that are SCN-free might form after the blue precipitate.

This reaction provides a new specific qualitative test for the Cu^{II} with a sensitivity of 1/500,000 ($10^{-5.7}$).

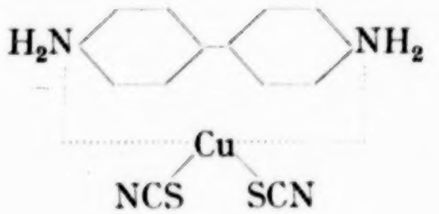
As this reaction is only given by *o*-benzidinemonosulfonic acid among the three benzidinesulfonic acids we have studied, it can also be used to distinguish quickly the *o*-benzidinemonosulfonic acid from *o-o'*-disulfonic and *m-m'*-disulfonic acids. At the same time this behaviour is another proof of the influence of the $-SO_3H$ group on $-NH_2$ benzidinic groups. When two sulfonic groups are present it can even inhibit the reaction, showing an analogy with other substituants such as $-OCH_3$ in the reactivity of *o*-dianisidine with regard to the benzidine.

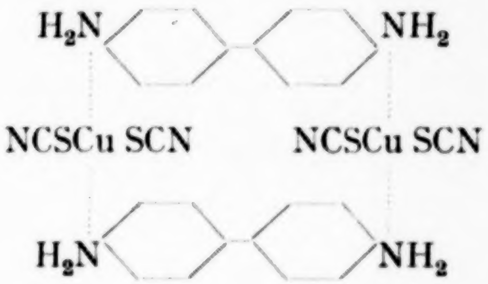
We did not use this reaction for the gravimetric estimation of copper in spite of its high sensitivity, as it is very difficult to obtain a readily filtrable precipitate without any loss of Cu^{II}, this being due to its easy peptization. Peptization is increased by the presence of an excess of reagent, but this excess is essential to ensure a complete precipitation of the copper. It may be possible, however, to use the reaction as a base for a colorimetric method.

Considerations about the possible mechanism of the reaction

This is just one of the problems concerning the formation of blue precipitates by various aromatic amines under the same conditions, for which different interpretations have been proposed.

The precipitate given by benzidine and copper salts, thiocyanates being present, has been studied by SPACU[4,5] who proposed, as possible formulae of these compounds, the following complex formulae:





We studied the reaction given by *o*-dianisidine under the same conditions[6] and we indicated this possible formula (Cu-*o*-dian) $(SCN)_2$.

The reaction of *α*-naphtylamine under the same conditions was also studied by us[7] and the formation of meriquinoid compounds by means of oxydation was admitted as possible.

It has not yet been decided whether the mechanism of the reaction involves the formation of complex salts as was originally proposed by SPACU, or whether it might be an oxidation process of the amine leading to the formation of a blue meriquinoid compound, as proposed by TETTAMANZI AND FEIGL in the case of benzidine, and by ourselves in the case of *α*-naphtylamine. In a similar reaction when potassium mercuric thiocyanate is present, SIERRA is rather inclined to admit the formation of complexes.

There are many arguments for and against both theories. On the one hand there are some non-oxidizable substances that yield blue products, as for instance, the pyridine giving blue precipitates with copper in presence of thiocyanate. But, on the other hand, if the reaction of many aromatic amines with cupric thiocyanate is carried out, it can be observed that blue precipitates are given only by amines that are easily oxidized by oxidizing agents — blue meriquinoid compounds being formed — while the non-oxidizable amines do not give such precipitates. For instance, benzidine, *o*-tolidine, *o*-dianisidine and *α*-naphtylamine, the reactions of which with the oxidizing agents are known, react well with SCN^- and Cu^{II}, but as we have indicated[7], *β*-naphtylamine does not. *β*-Naphtylamine also does not give the usual oxidizing reactions of its *α*-isomer.

The oxidizing action of cupric thiocyanate could be easily explained in view of its easy transformation into cuprous thiocyanate while sulfocyanogen is set free; this process appears to explain the high sensitivity that this sort of reaction provides if we bear in mind that:

a) oxidation leads to the formation of a product with a great coloring intensity.

b) the nascent sulfocyanogen is a pseudohalogen of considerable oxidizing power, intermediate between that of iodine and that of bromine.

References p. 404.

c) The formation of free sulfocyanogen is favoured by the small solubility product of cuprous thiocyanate ($4 \cdot 10^{-14}$) which is smaller than the solubility product of cuprous iodide ($1.1 \cdot 10^{-10}$). These considerations are in accordance with the following fact which we have checked experimentally: the reaction carried out either with benzidine or *o*-dianisidine with different copper halides (chloride, bromide, iodide and thiocyanate) is given by thiocyanate with maximum intensity.

This mechanism of oxidation has another test in its favour, *viz.* the behaviour of these three benzidine sulfonic acids. *o*-Monosulfonic acid which is the acid that more easily gives general oxidation reactions[1,2] is at the same time the only one that gives this special reaction with cupric thiocyanate. It seems permissible, in view of this fact, to consider that the reaction occurs in the simple manner of formation of a cuprous salt and a blue meriquinoid compound. This oxidation is probably already linked to the simultaneous formation of coordination complexes.

In addition to these observations there is also the fact that the precipitate does not show a perfectly defined composition but, on the contrary, if sufficient quantities of reagent are used, intermediate compounds are obtained whose percentage of copper is not constant and always greater than the percentage obtained when an excess of reagent is used.

On the other hand, the results given by the analysis of the precipitate do not justify (as shown in the experimental part) a formula of inner complex with two molecules of the reagent for one copper atom; neither do they meet the formulae SPACU suggested, as the difference between the results of the analysis and the theoretical values calculated for these formulae is so great that it could not be explained even by the great tendency of these blue precipitates to absorb the copper salts present.

EXPERIMENTAL PART

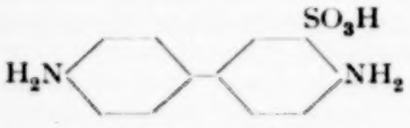
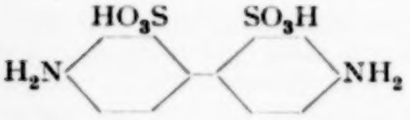
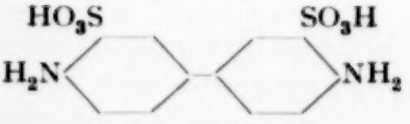
Solutions to be analysed. $1\,M$ Copper nitrate, copper chloride and copper sulfate solutions are used.

Reagent solution. (a) 15 g of purified benzidine-*o*-monosulfonic acid are weighed and transferred to a 500 ml capsule; 5 ml of NH_4OH are added drop by drop; the pulp thus formed takes slowly a reddish brown colour. If necessary 2 more ml are added, as well as 400 ml of distilled water. If the pH of the solution is greater than 7, one or two grams of solid reagent are added until the pH is brought down to the desired value. The solution is diluted to 1000 ml and after filtering the filtrate is used as a reagent.

(b) Normal solution of ammonium thiocyanate.

Qualitative behaviour of the three sulfonic acids

The reagent solutions of the *o-o'*-benzidinedisulfonic and *m-m'*-benzidinedisulfonic acids have been similarly prepared. Their behaviour with Cu^{II} has been studied (5 ml of $CuSO_4$ (1%) + 2 ml NH_4SCN + 3 ml of the reagent).

Salt of the acid	*In the cold*	*From hot solutions*
	Abundant blue precipitate soluble in NO_3H and NH_4OH	It agglomerates and turns greenish
	Nothing	Nothing
	After a few minutes a greenish cloudiness appears	

References p. 404.

Method for the identification of Cu^{II}. 2 drops of the solution under examination are deposited on a drop plate; the solution has been previously diluted just enough to avoid the precipitation of the copper with the thiocyanate; 3 drops of normal potassium thiocyanate and one drop of reagent are added. When Cu^{II} is present a blue coloring or a blue precipitate appears.

The precipitate is soluble in dilute mineral acids and in ammonium hydroxide and a further addition of alkalies or acids respectively does not produce its precipitation. It is insoluble in usual organic solvents. When heated it takes a greenish colour and when ignited it gives CuO.

Sensitivity of the reaction. The blue precipitate can be observed with a 1/100,000 concentration. The blue coloring persists and can be clearly seen with concentrations somewhat greater than 1/500,000. Therefore, the limit of the dilution can be considered to be $10^{-5.7}$.

Composition of the precipitate. Many precipitates have been prepared following the method indicated below and using copper chloride as unknown solution.

Preparation of the precipitate in view of its analysis. 100 ml of the solution of copper salt are diluted to 500 ml and heated to about 60-70° C. Immediately after the slow addition of 50 ml of the normal solution of thiocyanate, the reagent solution is added until the precipitation is complete. Care must be taken to keep on stirring to avoid absorption. (If an excess of reagent is not used, intermediate compounds might form which have a greater copper content than the precipitate being studied; that occurs possibly as a consequence of the strong absorption shown by these precipitates and the copper salts.)

The precipitate is filtered through a sintered glass crucible (G-4) washed with water and dried to constant weight at 105° C.

Copper estimation. Carried out by calcination up to CuO (Average: 16.4% Cu).

Sulphur estimation. The process consists of the oxidation according to Liebig's method, using potassium hydroxide and potassium nitrate. The sulfate is weighed as barium sulfate. (Average: 18.4% S).

Nitrogen estimation. Following Kjeldahl's method, modified by Jodlbauer. (Average: 11.1% N).

SUMMARY

In the present work a new method for the detection of copper(II) is described. It is based on the reaction of this ion with the alkali salts of *o*-benzidinemonosulfonic acid, alkali thiocyanate being present. The sensitivity of this test is 1/500,000 ($10^{-5.7}$); it is specific for the Cu^{+2} ion and can also be used to distinguish quickly the above-mentioned acid from the benzidine *o-o'*-disulfonic and benzidine *m-m'*-disulfonic acids. It is believed that the mechanism of the reaction can be explained by an oxidation process.

RÉSUMÉ

Le présent exposé traite d'une nouvelle méthode pour la recherche du cuivre(II), basée sur sa réaction avec les sels alcalins de l'acide *o*-benzidinemonosulfonique, en présence de thiocyanates alcalins. La sensibilité de cette réaction est de 1/500,000 ($10^{-5.7}$); l'essai est spécifique de l'ion Cu^{+2} et peut être aussi appliqué pour différentier rapidement l'acide précité des acides benzidine *o-o'*-disulfonique et *m-m'*-benzidine disulfonique. Il semble que le mécanisme de la réaction peut s'expliquer par un processus d'oxydation.

ZUSAMMENFASSUNG

In der vorliegenden Arbeit wird eine neue Methode für den Nachweis von Kupfer(II) entwickelt. Sie geht von der Reaktion dieses Ions mit den Alkalisalzen der *o*-Benzidin-monosulfosäure in Gegenwart von Alkalithiocyanaten aus. Die Empfindlichkeit von dieser Prüfungsmethode beträgt 1/500,000 ($10^{-5.7}$). Die Reaktion ist spezifisch für das Cu^{+2}-Ion und erlaubt die sofortige Unterscheidung der obengenannten Säure von Benzidin-*o-o'*-disulfosäure und -*m-m'*-disulfosäure. Es scheint dass der Mechanismus der Reaktion mit Hilfe eines Oxydationsprozesses erklärt werden kann.

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DIETHYLENETETRA-AMMONIUM SULPHATOCERATE AS VOLUMETRIC REAGENT

II. IODINE MONOCHLORIDE METHOD. INDIRECT DETERMINATIONS*

by

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In acid medium diethylenetetra-ammonium sulphatocerate, $[Ce(NH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2)_2](SO_4)_2.2H_2SO_4.7H_2O$, reacts with potassium iodide:

$$2\ Ce^{+4} + I^- = 2\ Ce^{+3} + I^+$$

In presence of hydrochloric acid, potassium iodide reacts with potassium iodate, potassium metaperiodate, potassium dichromate, potassium bromate, ceric sulphate, hydrogen peroxide, lead dioxide and chloramine-B according to the following equations:

$$\begin{aligned}
IO_3^- + 2\ I^- + 6\ H^+ &= 3\ I^+ + 3\ H_2O \\
IO_4^- + 3\ I^- + 8\ H^+ &= 4\ I^+ + 4\ H_2O \\
Cr_2O_7^{-2} + 3\ I^- + 14\ H^+ &= 3\ I^+ + 2\ Cr^{+3} + 7\ H_2O \\
BrO_3^- + 3\ I^- + 6\ H^+ &= 3\ I^+ + Br^- + 3\ H_2O \\
2\ Ce^{+4} + I^- &= I^+ + 2\ Ce^{+3} \\
O_2^{-2} + I^- + 4\ H^+ &= I^+ + 2\ H_2O \\
PbO_2 + I^- + 4\ H^+ &= I^+ + Pb^{+2} + 2\ H_2O \\
C_6H_5SO_2N(Na)Cl + I^- + 2\ H^+ &= I^+ + C_6H_5SO_2NH_2 + NaCl
\end{aligned}$$

The reactions have been utilized for the quantitative determination of the substances.

EXPERIMENTAL

A known amount of each substance was transferred to a conical flask, and 5 ml of chloroform, a known excess of potassium iodide solution and enough hydrochloric acid to keep its normality between 4*N* to 6*N* were added. The excess of potassium iodide was titrated with diethylenetetra-ammonium sulphatocerate (DTS) solution. The reagent was added from a burette until the solution which was coloured with iodine became pale yellow and the chloroform layer acquired a purple colour. The conical flask was stoppered and vigorously shaken during the titration. Addition of small volumes of the sulphatocerate solution was continued, shaking vigorously after each addition, until the chloroform layer was faintly violet. The sulphatocerate solution was then added dropwise, with shaking after the addition of each drop, till the chloroform layer became pale yellow. The end-point was very sharp.

Several titrations were performed in each case. From the volume of diethylenetetra-ammonium sulphatocerate (DTS) used, corresponding to the end-point in each titration, the amount of each substance was calculated. The results are recorded in Tables I-VIII. From these results it is con-

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cluded that diethylenetetra-ammonium sulphatocerate (DTS) can be used as a volumetric reagent to determine indirectly potassium iodate, potassium metaperiodate, potassium dichromate, potassium bromate, ceric sulphate, hydrogen peroxide, lead dioxide and chloramine-B by the iodine monochloride method.

All chemicals, except ceric sulphate and chloramine-B, used in this investigation were of guaranteed purity. Ceric sulphate was standardized with ferrous ethylenediamine sulphate. Chloramine-B was freshly prepared and standardized by an iodometric method.

TABLE I

POTASSIUM IODATE

KIO_3 taken g	*0.02N KI added* ml	*0.02N DTS used for excess KI* ml	*0.02N KI used by KIO_3* ml	*KIO_3 found* g
0.0092	30.00	21.40	8.60	0.0092
0.0123	30.00	18.50	11.50	0.0123
0.0153	30.00	15.70	14.30	0.0153
0.0189	30.00	12.30	17.70	0.0189
0.0215	30.00	9.90	20.10	0.0215

TABLE II

POTASSIUM METAPERIODATE

KIO_4 taken g	*0.02N KI added* ml	*0.02N DTS used for excess KI* ml	*0.02N KI used by KIO_4* ml	*KIO_4 found* g
0.0069	30.00	21.00	9.00	0.0069
0.0092	30.00	18.00	12.00	0.0092
0.0119	30.00	14.50	15.50	0.0119
0.0138	30.00	12.00	18.00	0.0138
0.0163	30.00	8.80	21.20	0.0163

TABLE III

POTASSIUM DICHROMATE

$K_2Cr_2O_7$ taken g	*0.02N KI added* ml	*0.02N DTS used for excess KI* ml	*0.02N KI used by $K_2Cr_2O_7$* ml	*$K_2Cr_2O_7$ found* g
0.0083	30.00	21.50	8.50	0.0083
0.0108	30.00	19.00	11.00	0.0108
0.0140	30.00	15.70	14.30	0.0140
0.0169	30.00	12.80	17.20	0.0169
0.0210	30.00	8.60	21.40	0.0210

TABLE IV

POTASSIUM BROMATE

$KBrO_3$ g	*0.02N KI added* ml	*0.02N DTS used for excess KI* ml	*0.02N KI used by $KBrO_3$* ml	*$KBrO_3$ found* g
0.0056	30.00	20.00	10.00	0.0056
0.0072	30.00	17.00	13.00	0.0072
0.0091	30.00	13.60	16.40	0.0091
0.0114	30.00	9.55	20.45	0.0114
0.0128	30.00	7.05	22.95	0.0125

TABLE V

CERIC SULPHATE

$Ce(SO_4)_2$ taken g	0.02N KI added ml	0.02N DTS used for excess KI ml	0.02N KI used by $Ce(SO_4)_2$ ml	$Ce(SO_4)_2$ found g
0.0618	30.00	20.70	9.30	0.0618
0.0811	30.00	17.80	12.20	0.0811
0.0997	30.00	15.00	15.00	0.0997
0.1196	30.00	12.00	18.00	0.1196
0.1475	30.00	7.90	22.10	0.1469

TABLE VI

HYDROGEN PEROXIDE

H_2O_2 taken g	0.02N KI added ml	0.02N DTS used for excess KI ml	0.02N KI used by H_2O_2 ml	H_2O_2 found g
0.0044	30.00	17.00	13.00	0.0044
0.0053	30.00	14.50	15.50	0.0053
0.0062	30.00	11.80	18.20	0.0062
0.0073	30.00	8.65	21.35	0.0073
0.0089	30.00	3.95	26.05	0.0089

TABLE VII

LEAD DIOXIDE

PbO_2 taken g	0.02N KI added ml	0.02N DTS used for excess KI ml	0.02N KI used by PbO_2 ml	PbO_2 found g
0.0239	30.00	20.00	10.00	0.0239
0.0311	30.00	17.00	13.00	0.0311
0.0383	30.00	14.00	16.00	0.0383
0.0454	30.00	11.00	19.00	0.0454
0.0502	30.00	9.00	21.00	0.0502

TABLE VIII

CHLORAMINE-B

$C_6H_5SO_2N(Na)Cl.3H_2O$ taken g	0.02N KI added ml	0.02N DTS used for excess KI ml	0.02N KI used by $C_6H_5SO_2N(Na)Cl.3H_2O$ ml	$C_6H_5SO_2N(Na)Cl.3H_2O$ found g
0.0187	30.00	23.00	7.00	0.0187
0.0294	30.00	19.05	10.95	0.0293
0.0385	30.00	15.65	14.35	0.0384
0.0463	30.00	12.75	17.25	0.0461
0.0586	30.00	8.10	21.90	0.0586

SUMMARY

In presence of 4*N* to 6*N* hydrochloric acid, diethylenetetra-ammonium sulphatocerate was used as a volumetric reagent to determine indirectly potassium iodate, potassium metaperiodate, potassium dichromate, potassium bromate, ceric sulphate, hydrogen peroxide, lead dioxide and chloramine-B by the iodine monochloride method. An excess of potassium iodide added to each

of the substances in the acid medium was titrated back with a standard solution of diethylenetetra-ammonium sulphatocerate. Chloroform was used as an indicator. It was coloured violet owing to the liberation of iodine during the titration and became very pale yellow at the endpoint because of the formation of iodine monochloride.

RÉSUMÉ

Le sulfate de di(éthylènediamino)-cérium (IV), en présence d'acide chlorhydrique 4 à 6*N* a été utilisé comme réactif pour le dosage volumétrique indirect de l'iodate, du métaperiodate, du dichromate et du bromate de potassium, du sulfate cérique, du peroxyde d'hydrogène, du dioxyde de plomb et de la chloramine B, par la méthode au monochlorure d'iode. L'excès d'iodure de potassium, ajouté à chacune de ces substances, en milieu acide, est titré par une solution étalon de sulfate de di(éthylènediamino)-cérium(IV). Le chloroforme est utilisé comme indicateur; il se colore en violet par l'iode libéré pendant le titrage et devient jaune très pâle au point final par formation de monochlorure d'iode.

ZUSAMMENFASSUNG

Das Cer(IV)di(äthylendiamin)sulfat, wurde in Gegenwart von 4-6*N* Salzsäure als Reagenz für die indirekte volumetrische Bestimmung von Jodat, Metaperjodat, Bichromat, Kaliumbromat, Cersulfat, Wasserstoffperoxyd, Bleidioxyd und Chloramin B, nach der Jodmonochlorid-Methode verwendet. Der Überschuss an Kaliumjodid der zu jeder dieser Substanzen zugegeben wurde, wird in saurem Milieu mit einer Titerlösung von Cer(IV)di(äthylendiamin)sulfat titriert. Das Chloroform wird als Indikator verwendet. Es färbt sich violett durch das während der Titration in Freiheit gesetzte Jod und wird am Endpunkt durch die Bildung von Jodmonochlorid blassgelb.

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THE TITRATION OF NICKEL WITH EDTA AT pH 2.8

by

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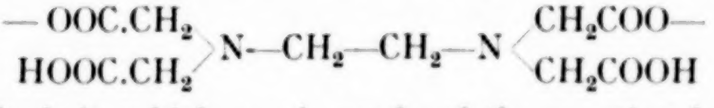
INTRODUCTION

In the present article the titration of nickel with EDTA (ethylenediaminetetraacetate) which can be regarded as a complex H_2Y^{-2}, where Y represents



$$\begin{matrix}-OOC.CH_2 \\ HOOC.CH_2\end{matrix}\!\!>N-CH_2-CH_2-N\!\!<\!\begin{matrix}CH_2COO- \\ CH_2COOH\end{matrix}$$

at pH 2.8 is described, in which use is made of the reaction between EDTA and thorium[1].

A small excess of EDTA is added to the nickel-containing solution, the pH is adjusted to about 2.8 and the excess is back-titrated with thorium nitrate, using alizarin-S as indicator.

SCHWARZENBACH and co-workers have determined the complex-forming constants of a number of elements[2]. For nickel they give

$$K_1 = \frac{(Ni^{+2})\ (Y^{-4})}{(NiY^{-2})} = 10^{-18.45} \text{ at } 20°\,C.$$

It is calculated from this that at pH 2.8, less than 0.1% of nickel is present as free ion, when equivalent quantities of Ni^{+2} and H_4Y are present.

The titration of nickel in the manner described above is thus highly feasible. The results may be expected to be somewhat low, since during the titration with thorium nitrate the secondary reaction $NiY^{-2} + Th^{+4} \leftrightarrows ThY + Ni^{+2}$ will also take place to some slight extent (the complex-formation of ThY is greater than that of NiY^{-2}, see below); but these exchange reactions appear to take place slowly, since our experiments have shown that any error due to them is small.

The nickel complex formed is blue in colour. We availed ourselves of this property for the rough spectrophotometric determination of the complex-forming constant of thorium with EDTA. Known quantities of nickel, thorium and EDTA were brought together, and the decrease in extinction measured; this at once shows that complex formation is greater with thorium than with nickel.

An advantage offered by the titration method is that it can be performed in the presence of cobalt. Quantities of Co up to 10 mg interfered hardly at all, so that the method permits the direct determination of nickel in the presence of cobalt.

EXPERIMENTAL PART

Reagents

All reagents were of c.p. grade. Deionized water (spec. resistance $> 10^6$ ohm) was used in the experiments. For the nickel determinations a nickel nitrate solution was used, the content of which had been determined gravimetrically as Ni-dimethylglyoxime.

The content was checked by

1. titration with EDTA for murexide at pH 11.5
2. acidimetrically after passage through a cation exchanger in H^+ form.

The maximum deviation in respect of the gravimetric method amounted to + or — 0.2%.

EDTA solution 0.05*M*:

Dissolve 18.6 g of ethylene diamine tetraacetic acid (disodium salt) and dilute to 1000 ml.

Thorium nitrate solution 0.05*M*:

Dissolve 27.6 g of $Th(NO_3)_4.4H_2O$ and dilute to 1000 ml. Both solutions are standardized by the method described in[1].

Alizarin-S indicator, 0.1%:

Dissolve 0.1 g of alizarin-S and dilute to 100 ml.

Monochloroacetic acid 2*M*:

Dissolve 189 g of $CH_2ClCOOH$ and dilute to 1000 ml.

Sodium acetate 1*M*:

Dissolve 136 g of $CH_3COONa.3H_2O$ and dilute to 1000 ml.

Method

A small excess (1-5 ml) of EDTA solution is added to the solution containing 1-4 m equiv. of Ni (30-120 mg). The solution is diluted to about 100 ml and neutralized with ammonia 2*N* against Congo red paper. 5 ml monochloroacetic acid solution and 5 ml sodium acetate solution are then added. The pH is checked and, if necessary, adjusted with ammonia or HCl 2*N* (pH limits 2.7-2.9).

1.5 ml of alizarin-S indicator solution are added, and immediately afterwards the excess of EDTA is back-titrated with thorium nitrate solution; the colour change from green to brown is very sharp.

A number of the values found by this method are reproduced in Table I.

TABLE I

TITRATION OF Ni WITH AN EXCESS OF EDTA AND BACK-TITRATION WITH THORIUM NITRATE AT pH 2.8

Ni present mg	*Ni found mg*	*Deviation in mg*
17.57	17.41	—0.16
	17.45	—0.12
35.14	35.14	0
52.71	52.72	+0.01
	52.72	+0.01
70.28	70.03	—0.25
	70.25	—0.03
99.4	99.3	—0.1
	99.7	+0.3

Influence of the pH

Good results were obtained in a pH interval varying from 2.6-4.3; at the latter pH (at which the titration is performed at the boiling temperature, see[1], the values for nickel lie 0-0.2% above the expected value.

A pH of 2.8 was selected, however, since then Mn and Co exert no influence. This is of importance in the analysis of steel.

Influence of excess of EDTA

A 10-50% excess of EDTA has no influence on the results, provided that during the back-titration the pH does not fall below 2.7.

The quantity of buffer solution has been chosen so that at an excess of 1 m equiv. of EDTA (0.5 mmol) the pH does not appreciably change during the back-titration with thorium nitrate.

Influence of other metal ions

Special attention was paid to the influence of cobalt, since the latter often occurs in combination with nickel. It appeared that even 10-20 mg of Co in combination with 100 mg of Ni produced only a slight (0.5-1%) excess value for nickel. The colour change is somewhat hesitant in this case, because the end-colour continuously recedes due to the exchange reaction

$$\text{Th-alizarin S} + \text{Co}Y^{-2} \leftrightarrows \text{Th}Y + \text{alizarin S} + \text{Co}^{+2}$$

The end-point is clearly perceptible, however, as a permanent colour change to brown.

In the presence of Co it is advisable to increase the volume of the solution to 175-200 ml; moreover additional indicator should be added (2.5 ml instead of 1.5 ml). The values given in Table II were determined in this way.

TABLE II

NICKEL WITH EXCESS EDTA AND BACK-TITRATION WITH THORIUM NITRATE IN THE PRESENCE OF Co (pH 2.6-2.8, VOLUME 175-200 ml, 2.5 ml INDICATOR SOLUTION)

mg Ni present	*mg Ni found*	*Deviation mg Ni*	*Further data*	
72.87	72.21	−0.66	5 mg Co	pH 2.6
	72.57	−0.30	,,	pH 2.7
	72.69	−0.18	,,	pH 2.8
	72.93	+0.06	,,	,,
	73.11	+0.24	10 mg Co	,,
101.6	102.1	+0.5	,,	,,
	102.0	+0.4	,,	,,
	102.4	+0.8	20 mg Co	,,
	102.2	+0.6	,,	,,

Although in the table only cobalt quantities of up to only 20 mg are cited, we have also made tests with up to 50 mg of Co in combination with 100 mg Ni. The deviations are then greater (2% relatively) and the determination of the end-point is rather difficult.

The fact that Co^{+2} affects the nickel titration to only a small extent must be attributed to its weaker tendency to complex-formation as compared with nickel ($K_{\text{Co}Y^{-2}} = 10^{-16.1}$, $K_{\text{Ni}Y^{-2}} = 10^{-18.45}$) whilst the great binding tendency of thorium to EDTA ($K_{\text{Th}Y} \approx 10^{-19.8}$) may also have a favourable influence.

Accordingly the influence of 10 mg of Zn ($K_{\text{Zn}Y^{-2}} = 10^{-16.15}$) is of the same order as that of Co. For 10 mg of Mn ($K_{\text{Mn}Y^{-2}} = 10^{-13.5}$) the influence is nil, as would be expected.

The influence of Pb, however, ($K_{\text{Pb}Y^{-2}} = 10^{-18.2}$) is fairly considerable. In the presence of 5 mg of Co, Zn and Pb in combination with 100 mg Ni for example, we found a 1% higher result, whilst in the presence of 50 mg of Zn and Pb the end-point could not even be distinctly determined.

Cu^{+2} ($K_{\text{Cu}Y^{-2}} = 10^{-18.38}$) reacts for 95% just as Al, whilst Fe^{+3} ($K_{\text{Fe}Y^{-2}} = 10^{-25.1}$) reacts quantitatively, just as Bi^{+3} ($K_{\text{Bi}Y^{-2}}$?).

Ca, Ba, Sr and Mg in quantities of 40 mg do not interfere (K greater than 10^{-11}).

For the influence of anions we refer the reader to a previous publication[3].

APPROXIMATE DETERMINATION OF THE COMPLEX-FORMING CONSTANT OF THORIUM WITH EDTA

The blue colour of the nickel complex was used to determine an approximate value for the complex-forming constant of Th-EDTA.

The principle was as follows:

Equivalent quantities of Ni and EDTA were brought together and varying quantities of thorium nitrate added. The pH was adjusted at 2.5-3.0, the solution made

0.1*N* to KCl and the whole diluted to 100 ml. The extinctions of the solutions thus obtained were measured after 12 hours' standing (the extinctions had then become constant, showing that equilibrium had been reached).

From the change in extinction the $(\mathrm{Ni}Y^{-2})$ could at once be determined, whilst the other concentrations could be calculated from the initial situation and the $(\mathrm{Ni}Y^{-2})$.

With the help of $K_{\mathrm{Ni}Y^{-2}} = 10^{-18.45}$ the value of $K_{\mathrm{Th}Y}$ was then found.

It was assumed in the calculation that the formation of $\mathrm{Ni}Y^{-2}$ and $\mathrm{Th}Y$ goes to completion; this is permissible in view of the very strong complex formation. The reaction, in which we were interested, can then be schematically represented by (a):

$$\mathrm{Ni}Y^{-2} + \mathrm{Th}^{+4} \leftrightarrows \mathrm{Th}Y + \mathrm{Ni}^{+2} \text{ with } K = \frac{(\mathrm{Th}Y)\ (\mathrm{Ni}^{+2})}{(\mathrm{Ni}Y^{-2})\ (\mathrm{Th}^{+4})}$$

and the latter reaction can be imagined to be composed of (b):

$$\mathrm{Ni}Y^{-2} \leftrightarrows \mathrm{Ni}^{+2} + Y^{-4} \text{ with } K_{\mathrm{Ni}Y^{-2}} = \frac{(\mathrm{Ni}^{+2})\ (Y^{-4})}{(\mathrm{Ni}Y^{-2})}$$

and (c):

$$\mathrm{Th}^{+4} + Y^{-4} \leftrightarrows \mathrm{Th}Y \text{ with } K_{\mathrm{Th}Y} = \frac{(\mathrm{Th}^{+4})\ (Y^{-4})}{(\mathrm{Th}Y)}$$

so that $K = \dfrac{K_{\mathrm{Ni}Y^{-2}}}{K_{\mathrm{Th}Y}}$ and consequently $\log K_{\mathrm{Th}Y} = \log K_{\mathrm{Ni}Y^{-2}} - \log K$

$(\mathrm{Ni}Y^{-2})$ was calculated directly as the proportion of the extinctions of the equilibrium- and initial conditions, E_e and E_s respectively, multiplied by the initial concentration of $\mathrm{Ni}Y^{-2}$ ($= C_{\mathrm{Ni}Y^{-2}}$). A small correction on E_e was carried out, because the Ni^{+2} liberated also absorbs slightly at the wavelength used. This correction was easily calculated from the extinction of a pure Ni^{+2} solution (see Table III).

It follows further from reaction (a):

$$(\mathrm{Ni}^{+2}) = C_{\mathrm{Ni}Y^{-2}} - (\mathrm{Ni}Y^{-2})$$
$$(\mathrm{Th}Y) = (\mathrm{Ni}^{+2})$$
$$(\mathrm{Th}^{+4}) = C_{\mathrm{Th}^{+4}} - (\mathrm{Th}Y)$$

(in which $C_{\mathrm{Th}^{+4}}$ is the added quantity of Th^{+4}).

TABLE III

EXTINCTION OF SOLUTIONS WITH EQUIVALENT QUANTITIES Ni^{+2} AND EDTA WITH VARYING QUANTITIES OF Th^{+4}

Milieu 0.1*N* KCl, pH 2.5-3, volume 100 ml. Temp. *ca.* 20° C. Wavelength 600 mμ, cell 30 mm

E_s	E_e	E_e *(corr.)*	$C_{\mathrm{Th}^{+4}}$	$(\mathrm{Ni}Y^{-2})$	(Ni^{+2})	(Th^{+4})	K
	0.340	0.334	$0.3395 \cdot 10^{-2}$	$1.358 \cdot 10^{-2}$	$0.337 \cdot 10^{-2}$	$0.0025 \cdot 10^{-2}$	33.4
	0.271	0.260	$0.6790 \cdot 10^{-2}$	$1.057 \cdot 10^{-2}$	$0.638 \cdot 10^{-2}$	$0.041 \cdot 10^{-2}$	9.4
	0.185	0.168	$1.0185 \cdot 10^{-2}$	$0.683 \cdot 10^{-2}$	$1.012 \cdot 10^{-2}$	$0.0065 \cdot 10^{-2}$	23.1
	0.109	0.087	$1.3580 \cdot 10^{-2}$	$0.354 \cdot 10^{-2}$	$1.341 \cdot 10^{-2}$	$0.017 \cdot 10^{-2}$	29.8
0.417	$1.695 \cdot 10^{-2}$ mol Ni^{+2}/l and $1.695 \cdot 10^{-2}$ mol EDTA/l						
0.000	$1.358 \cdot 10^{-2}$ mol Th^{+4}/l and $1.695 \cdot 10^{-2}$ mol EDTA/l						
0.030	$1.695 \cdot 10^{-2}$ mol Ni^{+2}/l in 0.1*N* KCl.						

From the K values thus found we calculate for log $K_{\mathrm{Th}Y}$:

$-18.45 - 1.52 = -19.97$ to 1 place of decimals -20.0
$-18.45 - 0.97 = -19.42$,, ,, ,, -19.4
$-18.45 - 1.36 = -19.81$,, ,, ,, -19.8
$-18.45 - 1.47 = -19.92$,, ,, ,, -19.9
average -19.8 ± 0.13

$$K_{\mathrm{Th}Y} = 10^{-19.8 \pm 0.13}$$

SUMMARY

A method for determining nickel using EDTA is described. A small excess of EDTA is added, the pH adjusted to 2.7-2.9 and the solution back-titrated with thorium nitrate, against alizarin-S as indicator. Quantities of cobalt up to 10 mg do not interfere.

In addition an approximate determination of the complex-forming constant of Th-EDTA is described, based on the decrease in extinction of an Ni-EDTA solution to which Th^{+4} has been added.

RÉSUMÉ

Une méthode est décrite pour le dosage du nickel au moyen de l'acide éthylènediaminotétra-acétique (EDTA). Un léger excès de réactif est ajouté, le pH est ajusté à 2.7-2.9 et la solution est titrée en retour par le nitrate de thorium, en présence d'alizarine-S comme indicateur. Des quantités de cobalt allant jusqu'à 10 mg ne gênent pas. On décrit également une détermination approximative de la constante de formation du complexe Th EDTA, basée sur la diminution de l'extinction d'une solution Ni-EDTA à laquelle on ajoute Th^{+4}.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben, um Nickel mittels der Äthylendiaminotetraessigsäure (EDTA) zu bestimmen. Ein leichter Überschuss des Reagenzes wird zugegeben, der pH auf 2.7-2.9 gebracht und die Lösung in Gegenwart von Alizarin-S als Indikator mit Thoriumnitrat zurücktitriert. Kobaltmengen bis zu 10 mg stören nicht. Beschrieben wird ebenfalls eine annähernde Bestimmung der Th-EDTA-Komplexbildungs-Konstante, welche auf der Verminderung der Extinktion einer Ni-EDTA-Lösung beruht, zu welcher man Th^{+4} zufügt.

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THE DETERMINATION OF ZIRCONIUM IN FLUORIDE-CONTAINING SOLUTIONS

by

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INTRODUCTION

The recently developed EDTA titration procedures for zirconium have proved extremely useful in the analysis of binary alloy systems. Thus the direct titration of zirconium is possible in the analysis of uranium-zirconium[1] and cerium-zirconium alloys[2]. With tantalum-zirconium and niobium-zirconium alloys the separation of the zirconium from the earth acid constituent was found to be desirable[3]. This was accomplished by the solvent extraction of most of the earth acid element into hexone from a fluoride solution of the sample. The zirconium was finally separated from small amounts of unextracted tantalum or niobium by precipitation with ammonium hydroxide in the presence of hydrogen peroxide, the earth acid elements remaining in solution as peroxy complexes under these conditions. In the analysis of ternary alloy systems for zirconium by the EDTA procedure, the preliminary separation of the zirconium from other alloying constituents appeared desirable. A technique was required that was reasonably specific for zirconium and was also directly applicable to fluoride-containing solutions. This latter requirement arose because of the need to use hydrofluoric acid in effecting the complete solution of zirconium-containing alloys.

Zirconium can be readily precipitated from fluoride solutions as insoluble barium fluozirconate. This precipitation was first employed by HUME[4] in the analysis of fission products and TELFORD[5] later used this technique in the analysis of uranium-niobium-zirconium alloys. In this latter work, zirconium in the range 50 to 150 mg was precipitated as barium fluozirconate and separated by filtration on a Whatman No. 42 filter paper. This precipitate was redissolved in a mixture of boric and hydrochloric acids, the zirconium being recovered from solution by precipitation with cupferron. After filtration, the cupferride precipitate was finally ignited to zirconium oxide. It is assumed that TELFORD took sample weights containing more than 50 mg of zirconium to give reasonable amounts of zirconium oxide to weigh at the end of the determination. This precipitation technique appeared very suitable for the preliminary separation of zirconium in complex alloy analysis before the application of the EDTA titration. Moreover, the use of the volumetric procedure would eliminate the need to take sample weights containing more than 50 mg of zirconium, since it is readily applicable to amounts of zirconium of the order of a few milligrams. However, information was needed on the optimum solution conditions for the quantitative precipitation of the zirconium and on the behaviour of other elements in this process, although TELFORD's work showed conclusively that uranium and niobium do not interfere. Data on these points have been obtained in our study and are reported in this paper.

EXPERIMENTAL

The solvent acids needed for the solution of most ternary alloys can be expected to be hydrofluoric, nitric and hydrochloric acids in various combinations. In preliminary experiments therefore the precipitation of barium fluozirconate was studied from HNO_3 + HF and HCl + HF mixtures. Sulphuric acid clearly could not be used as a solvent acid in this work because of the simultaneous precipitation of barium sulphate with barium fluozirconate. In the precipitation experiments from nitric acid solutions, a suitable volume of a standard zirconyl nitrate solution was placed in a transparent plastic centrifuge tube together with a measured volume of nitric acid (sp.gr. 1.42) and the solution was diluted with water to a volume of 20 ml. Then 10 ml of a 5% w/v barium nitrate solution was added, followed by 2 ml of hydrofluoric acid (40%) with stirring. After centrifuging for 5 minutes, the completion of precipitation was tested by the addition of further small quantities of barium nitrate and hydrofluoric acid, followed by further centrifuging if necessary. The supernatant liquid was removed by means of a polythene suction line over the end of which a small piece of filter paper was held in position by a polythene ring. Any precipitate adhering to the paper was simply removed by washing.

The precipitate was then transferred quantitatively to a beaker containing 10 ml of hydrochloric acid (sp.gr. 1.16), 10 ml of 5% boric acid and 75 ml of water. After boiling for 10-15 minutes the solution was returned to the centrifuge tube and made alkaline by the addition of ammonium hydroxide. The zirconium hydroxide precipitate was recovered by centrifuging, dissolving in a small amount of hydrochloric acid (1+1) and then evaporating to fumes of 20 ml of perchloric acid (60%) to ensure the complete removal of fluoride ions. The zirconium was then determined volumetrically by the addition of a slight excess of EDTA and back titrating at pH 5 to 6 with a standard iron solution, using salicylate as the indicator. Quantitative recoveries were obtained for zirconium from solutions up to 3*N* in nitric acid at the precipitation stage, whereas slightly low figures were obtained from solutions 5*N* in nitric acid. Typical results for the recovery of zirconium in amounts up to 100 mg are given in Table I.

TABLE I

RECOVERY OF ZIRCONIUM FROM NITRIC ACID SOLUTIONS

Normality of nitric acid in solution	*Wt of zirconium taken (mg)*	*Wt of zirconium recovered (mg)*
5.0	3.9	3.0
3.0	3.9	4.0
1.0	3.9	4.0
1.0	10.0	10.1
1.0	19.9	19.8
1.0	39.9	39.95
1.0	59.8	59.75
1.0	99.7	99.2

The above experiments were repeated in hydrochloric acid solutions, using barium chloride instead of the barium nitrate solution. The results in Table II show that the precipitation of barium fluozirconate is equally effective in hydrochloric acid media, complete recoveries being obtained from acid concentrations up to at least 3*N*.

TABLE II

RECOVERY OF ZIRCONIUM FROM HYDROCHLORIC ACID SOLUTIONS

Normality of hydrochloric acid	*Wt of zirconium taken (mg)*	*Wt of zirconium recovered (mg)*
0.5	20.0	20.1
1.0	20.0	19.9
3.0	20.0	20.1
5.0	20.0	19.7
7.5	20.0	Low and erratic recoveries

The barium fluozirconate precipitates were not washed in the above investigation. This process was purposely omitted because the experiments were carried out on pure zirconium solutions. With alloy solutions, however, it was necessary to wash the zirconium precipitates and work was therefore undertaken to develop a suitable washing technique. TELFORD simply washed the barium fluozirconate precipitates with water, but our experience showed that slight loss of zirconium could occur. We obtained better results by using a wash solution 1% w/v in barium nitrate, 2% v/v in hydrofluoric acid and 10% v/v in nitric acid, the composition of this solution approximately simulating that of the supernate. The wash solution finally chosen for this work had also been in contact with barium fluozirconate. A small amount of zirconium was included in the preparation of the solution and the precipitated barium fluozirconate was removed by filtration before use.

THE BEHAVIOUR OF OTHER ELEMENTS IN THE BARIUM FLUOZIRCONATE PRECIPITATION

Details are given here of the behaviour of other elements in the zirconium procedure. High purity zirconium metal (0.04% Hf by spectrographic analysis) was used throughout. This investigation was limited, however, to metals normally used in non-ferrous alloy systems. In some cases, where the other constituent was known to react with EDTA under the conditions for the titration of zirconium, a double precipitation of the latter was undertaken. To enable this second precipitation to be carried out, the first barium fluozirconate precipitate from solutions $2M$ in HF and less than $3M$ in HNO_3 was dissolved with stirring in 2 to 3 ml of saturated boric acid and about 10 ml of hot 20% nitric acid. This solution was diluted to 20 ml with water and the second precipitation of barium fluozirconate effected by the addition of 10 ml of 5% barium nitrate and 2 to 3 ml of hydrofluoric acid. In this study a recently improved procedure[6] for zirconium was also substituted for the visual method using salicylic acid as the indicator. In this method the titration of the excess of EDTA is carried out at pH 2.3 and a photoelectric absorptiometer is used to determine the end-point.

a) *Niobium and tantalum*

Specpure niobium metal and tantalum metallic sheet of 99.9% purity was used in this work, weighed amounts being dissolved in a few ml of (1+1) nitric acid by the dropwise addition of hydrofluoric acid. After the transference of these solutions to plastic centrifuge tubes, measured amounts of a gravimetrically standardized zirconyl nitrate solution were added. These solutions were then treated with barium nitrate and hydrofluoric acid to effect precipitation of barium fluozirconate. On re-solution in nitric-boric acids after a single precipitation, turbidities were often produced due to the hydrolysis of small amounts of co-precipitated niobium or tantalum. The addition of 1 or 2 drops of hydrogen peroxide (100 vols.) readily removed this cloudiness before the re-precipitation of the barium fluozirconate was carried out. The results obtained for the determination of 21.9 mg amounts of zirconium in the presence of varying amounts of niobium and tantalum up to a maximum of 1 g are given in Table III. Under these conditions there is clearly no interference from the earth acid elements.

TABLE III

DETERMINATION OF ZIRCONIUM IN THE PRESENCE OF NIOBIUM OR TANTALUM

Wt of Zr taken (mg)	*Wt of earth acids taken (mg)*	*Wt of Zr recovered (mg)*
21.9	250 Nb	22.1
21.9	500 Nb	22.1
21.9	1,000 Nb	22.0
21.9	250 Ta	22.0
21.9	500 Ta	21.9
21.9	1,000 Ta	22.0

b) *Tungsten*

Tungsten metal of 99.9% purity was dissolved in nitric-hydrofluoric acids for these tests. On re-solution of the barium fluozirconate in nitric-boric acids, a small yellow precipitate of tungstic acid was sometimes visible, especially in the separation of small amounts of zirconium from large amounts of tungsten. A little tungstic acid sometimes passed through to the final solution prior to titration. In these cases, the precipitate was removed by centrifuging and it was also washed with hydrochloric acid. The supernate and washes were combined and evaporated to fumes of perchloric acid in the ordinary way before carrying out the titration. The non-interference of tungsten was confirmed in this work; in a typical experiment 49.4 mg of zirconium were combined with 1 g of tungsten and a zirconium recovery of 49.5 mg was obtained.

c) *Titanium, uranium, molybdenum, lead, iron and copper*

The recovery of 20 mg and other amounts of zirconium in the presence of amounts up to 1 g of lead, copper, iron and uranium showed that no serious difficulties arose from these elements. In the experiments with molybdenum and titanium, the maximum amount taken of each element was 500 mg and 850 mg respectively. No interference was encountered and no trouble is envisaged from the presence of larger quantities. Results are given in Table IV.

d) *Aluminium and bismuth*

Although aluminium forms strong soluble fluoride complexes, an insoluble precipitate was formed in the presence of barium ions. Bismuth also precipitated from solution, presumably as its oxyfluoride, when the amount of bismuth exceeded 50 mg in the 30 ml of solution needed for the precipitation of barium fluozirconate.

Any bismuth accompanying the barium fluozirconate precipitate also consumes EDTA in the zirconium titration procedure and thereby leads to high results. The barium fluozirconate technique is therefore not suitable for the determination of zirconium in any alloy systems containing either bismuth or aluminium.

TABLE IV

DETERMINATION OF ZIRCONIUM IN THE PRESENCE OF Ti, U, Mo, Pb, Fe AND Cu

Wt of Zr taken (mg)	*Wt of other constituent (mg)*	*Wt of Zr recovered (mg)*
13.2	100 Ti	13.3
13.2	250 Ti	13.0
50.7	250 Ti	50.6
50.7	500 Ti	50.8
148.0	850 Ti	148.0
9.4	1000 U	9.1
39.9	1000 U	39.8
99.7	1000 U	99.8
12.5	500 U	12.3
19.0	500 U	18.9
64.1	116 U	64.3
5.0	500 Mo	5.0
31.1	500 Mo	30.6
15.8	87.5 Mo	16.0
21.2	1000 Pb	21.9
21.2	500 Pb	22.1
21.2	250 Pb	22.2
20.4	1000 Fe	21.4
20.4	500 Fe	21.5
20.4	250 Fe	21.6
20.0	1000 Cu	20.1
20.0	500 Cu	20.8
20.0	250 Cu	20.2

e) *Tin*

In this case the precipitation of the barium fluozirconate had to be carried out from hydrochloric acid solutions, nitric acid being completely unsuitable because of the formation of metastannic acid. Under these conditions it was also necessary to add 1 or 2 drops of hydrogen peroxide to inhibit the formation of a precipitate. The recovery of 20.0 mg amounts of zirconium from various quantities of tin up to a maximum of 1 g showed that there was no interference from this element. For example, zirconium recoveries of 20.3, 20.1 and 20.4 mg were obtained in the presence of 250, 500 and 1000 mg amounts of tin.

THE DETERMINATION OF ZIRCONIUM IN ALLOY SYSTEMS

The procedure outlined in the previous section has been used for the determination of zirconium in several uranium base ternary alloy systems. The alloys under investigation were uranium-titanium-zirconium, uranium-niobium-zirconium and uranium-molybdenum-zirconium. Solutions of these materials can be attained by the judicious use of nitric acid and small amounts of hydrofluoric acid. After evaporation to ensure the removal of most of the free mineral acid from the sample solution, the barium fluozirconate precipitation procedure can be applied directly and the zirconium content determined volumetrically with EDTA Details of the procedure applicable to alloy systems are as follows:

1. *Apparatus*

Platinum dishes *ca.* 3" in diameter are needed for the solution of alloys and transparent plastic centrifuge tubes (60 ml capacity) for the precipitation of barium fluozirconate. The fluoride containing solutions are mixed with polythene rods 4 mm in diameter.

An Eel photoelectric absorptiometer is suitable for the back-titration of the excess EDTA with a standard iron solution.

2. *Reagents*

a) Wash Solution — prepare a solution 1% w/v barium nitrate, 2% v/v hydrofluoride acid and 10% v/v nitric acid. Add a zirconium nitrate solution containing a few milligrams of zirconium and allow the barium fluozirconate precipitate to settle. Filter the solution and store in a polythene bottle.

b) Iron solution (0.1*M*) — dissolve 5.585 g of "specpure" iron in 20 ml of warm hydrochloric acid (sp.gr. 1.16). Dilute with water and completely oxidize by the careful dropwise addition of nitric acid (sp.gr. 1.42). Dilute to 1 litre with water.

c) EDTA solution (0.1*M*) — dissolve 37.23 g of the disodium salt of ethylenediamine tetra-acetic acid in water and dilute to 1 litre. Standardize this solution by accurately pipetting 25 ml into a 400 ml squat type beaker and diluting to a volume of about 300 ml with water. Adjust the pH of this solution to a value of 2.3 and position the beaker in the absorptiometer. Add 1 ml of a 2% potassium benzohydroxamate solution, stir the solution mechanically and adjust the absorptiometer reading to zero with Ilford 605 filters in position. Carry out the titration by addition of the standard iron solution from a calibrated burette, measuring the absorbancy at points before and after the end-point. Keep the glass electrode in the solution and re-adjust the pH to 2.3 from time to time throughout the titration. Plot a graph of the volume of iron solution added against absorbancy and determine the end-point from the intersection of the two straight line portions of the graph.

3. *Procedure*

Take a suitable weight of sample (approx. 1 g) in the form of drillings or millings in a *ca.* 3" covered platinum dish. Attack with about 20 ml of warm nitric acid (1+1) and add a few drops of hydrofluoric acid to assist solution. If a complete solution is produced, evaporate to a volume of about 2 ml. With samples producing a greenish precipitate of uranium tetrafluoride, add a small quantity of perchloric acid and fume strongly to decompose the precipitate, reducing the volume of the solution to about 2 ml by evaporation as before.

Transfer the sample solution to a centrifuge tube with water, but keeping the volume down to 20 ml. Then add 10 ml of a 5% w/v barium nitrate solution and 2 ml of hydrofluoric acid (40%). Allow to stand for 5 to 10 minutes, before centrifuging. At this stage add a further two drops of hydrofluoric acid to test for the complete precipitation of the zirconium. Remove the supernate by the special polythene suction line with a piece of filter paper covering the end and held in position by a polythene ring. Wash any precipitate adhering to the paper back into the centrifuge tube with water. Add 10 ml of the wash solution to the centrifuge tube and break up the precipitate using a polythene rod. Re-centrifuge and remove the solution as before. Dissolve the precipitate in 2 to 3 ml of saturated boric acid and about 10 ml of hot 20% v/v nitric acid, stirring to assist solution.

Re-precipitate the barium fluozirconate by the addition of 10 ml of 5% barium nitrate solution and 2 to 3 ml of hydrofluoric acid (40%). Repeat the centrifuging and washing of this precipitate as before dissolving in the boric-nitric acid mixture. Dilute this solution with water to a volume of approximately 30 ml and make ammoniacal to precipitate zirconium hydroxide. Centrifuge and remove the supernate. Then using a stirring rod wash the precipitate with 10-15 ml of hot 2% ammonium chloride. Centrifuge and remove the supernatant liquor as before. Dissolve the precipitate in 10 ml of hot hydrochloric acid (1+1), transfer the solution to a 400 ml squat beaker and evaporate to fumes of 20 ml of perchloric acid (60%). After strong fuming for 5-10 minutes, cool and wash the sides of the beaker with water. Then repeat the fuming process to ensure the complete removal of fluoride ions.

Continue fuming to reduce the volume of perchloric acid to about 2 to 3 ml. Then dilute the solution with 25 to 50 ml of water and add the slight excess of standard EDTA solution to complex the zirconium without delay. Dilute to a volume of 300 ml with water, adjust the pH to 2.3, add 1 ml of the 2% benzohydroxamate solution and carry out the back titration of the excess EDTA with the standard iron solution exactly as described in the procedure for the standardization of the EDTA solution. Maintain the glass electrode in the solution and readjust the pH from time to time during the titration as required. Calculate the zirconium content from the amount of EDTA consumed, 1 ml of 0.1 M EDTA = 9.122 mg of Zr.

RESULTS AND CONCLUSIONS

The above procedure has been tested by applying it to the determination of the zirconium content of synthetic ternary uranium base alloys, including the uranium-molybdenum-zirconium, uranium-titanium-zirconium and uranium-niobium-zirconium systems. In the first system the molybdenum varied from 5 to 15%, the zirconium from 1 to 10%, whilst the uranium was always greater than 75%. Both the titanium and zirconium contents of the second system were in the range 1 to 15% and the uranium was greater than 85%. With the third type of alloys, the uranium was in the range 50 to 80%, whilst the niobium and zirconium varied from 1 to 40%. Synthetic solutions of these alloys were prepared by dissolving suitable amounts of the respective pure metals in nitric and hydrofluoric acids in platinum dishes. These solutions were evaporated to volumes of about 2 ml before transference to a centrifuge tube and precipitation of the barium fluozirconate. The recovery results for zirconium are given in Tables V, VI and VII and in all cases a good agreement is shown between the amount of zirconium taken and the amount finally recovered.

TABLE V

ANALYSIS OF SYNTHETIC URANIUM-MOLYBDENUM-ZIRCONIUM ALLOYS

Zirconium (%)	*Wt of Zr taken (mg)*	*Uranium (approx. %)*	*Molybdenum (approx. %)*	*Wt of Zr in alloy by analysis (mg)*	*Zr in alloy by analysis %*	*Error in Zr determination %*
1.1	10.9	84	15	10.8	1.1	nil
1.1	10.8	94	5	10.8	1.1	nil
5.0	49.8	85	10	49.3	4.9	−0.1
5.1	50.5	90	5	50.1	5.0	−0.1
9.9	49.5	82	8	49.1	9.8	−0.1
10.1	50.6	75	15	50.2	10.0	−0.1

TABLE VI

ANALYSIS OF SYNTHETIC URANIUM-TITANIUM-ZIRCONIUM ALLOYS

Zirconium %	*Wt of Zr taken (mg)*	*Uranium (approx. %)*	*Titanium (approx. %)*	*Wt of Zr in alloy by analysis (mg)*	*Zr in alloy by analysis %*	*Error in Zr determination %*
1.0	10.0	85	14	10.0	1.0	nil
4.1	20.4	86	10	20.7	4.1	nil
7.1	35.1	85	8	34.7	7.0	−0.1
7.3	36.3	85	8	36.0	7.2	−0.1
13.9	69.2	85	1	68.4	13.7	−0.2
14.4	72.1	85	1	71.7	14.3	−0.1

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TABLE VII

ANALYSIS OF SYNTHETIC URANIUM-NIOBIUM-ZIRCONIUM ALLOYS

Zirconium (%)	*Wt of Zr taken (mg)*	*Uranium (approx. %)*	*Niobium (approx. %)*	*Wt of Zr in alloy by analysis (mg)*	*Zr in alloy by analysis %*	*Error in Zr determination %*
1.1	11.3	60	39	10.6	1.1	nil
10.1	50.3	80	10	50.3	10.1	nil
10.1	50.8	50	40	50.9	10.1	nil
15.2	76.1	65	20	76.1	15.2	nil
18.9	94.6	80	1	93.8	18.8	−0.1
25.0	100.1	50	25	99.4	24.8	−0.2
29.7	59.3	50	20	59.4	29.7	nil
38.9	77.6	60	1	77.2	38.7	−0.2

It can be concluded that the precipitation of zirconium as barium fluozirconate is a very useful technique for the separation of zirconium from other constituents in the analysis of uranium base alloys. After this separation, the ethylenediaminetetra-acetic acid procedure for zirconium is readily applicable with an appreciable saving in time when compared with the gravimetric method. Although the application of this new technique has been limited in this work to the analysis of uranium ternary base alloys, this procedure should help to simplify the determination of zirconium in other types of materials.

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SUMMARY

In the recommended procedure the zirconium is first precipitated from solution as the insoluble barium fluozirconate. After separation, the precipitate is dissolved in a mixture of nitric and boric acids and the zirconium is then precipitated as its hydroxide. This precipitate is separated, dissolved in hydrochloric acid and this solution is evaporated to fumes of perchloric acid to remove completely fluoride ions. The zirconium content is then determined volumetrically by adding a slight excess of a standard solution of ethylenediaminetetra-acetic acid and back titrating with a standard iron solution at pH 2.3 using potassium benzohydroxamate as indicator and the photometric technique for end-point detection. This method is applicable to the determination of milligram amounts of zirconium in fluoride-containing nitric or hydrochloric acid solutions provided that the concentration of these acids is below $3N$. It is also suitable for the determination of zirconium in the presence of any of the following elements — uranium, titanium, niobium, tantalum, molybdenum, tungsten, lead, iron, copper and tin.

RÉSUMÉ

Dans le procédé recommandé, le zirconium est d'abord précipité comme fluozirconate de baryum. Après séparation, le précipité est dissous dans un mélange d'acides nitrique et borique; le zirconium est ensuite reprécipité comme hydroxyde. Le précipité obtenu est séparé, dissous dans l'acide chlorhydrique, la solution est évaporée jusqu'à obtention des vapeurs d'acide perchlorique pour éliminer complètement les ions fluorhydriques. La teneur en zirconium est ensuite déterminée volumétriquement par addition d'un léger excès de solution étalon d'acide éthylènediaminotétraacétique. L'excès est titré par une solution étalon de fer au pH 2.3, en utilisant le benzohydroxamate de potassium comme indicateur et la technique photométrique pour déterminer le point final. Cette méthode permet le dosage du zirconium dans des solutions d'acide nitrique ou chlorhydrique renfermant un fluorure, à condition que la concentration de ces acides soit inférieure à $3N$. Elle permet également le dosage du zirconium en présence d'uranium, de titane, de niobium, de tantale, de molybdène, de tungstène, de plomb, de fer, de cuivre et d'étain.

References p. 422.

ZUSAMMENFASSUNG

Im beschriebenen Verfahren wird Zirkonium zuerst als unlösliches Bariumfluorozirkonat gefällt. Nach der Abtrennung wird das Präzipitat in einer Mischung von Salpetersäure und Borsäure gelöst; dann wird das Zirkonium als Hydroxyd gefällt. Der erhaltene Niederschlag wird abgetrennt und in Salzsäure gelöst. Die Lösung wird bis zur Entwicklung von Perchlorsäurenebel verdampft um die Fluorionen vollständig zu vertreiben. Der Zirkonium-Gehalt wird dann volumetrisch durch Hinzufügen eines kleinen Überschusses einer eingestellten Äthylendiamintetraessigsäurelösung und nachheriger Rücktitration mit einer eingestellten Eisenlösung bei pH 2.3 und mit Kaliumbenzohydroxamat als Indikator bestimmt. Für die Bestimmung des Endpunktes wird die photometrische Technik angewendet. Die Methode wird für die Bestimmung von Milligrammengen von Zirkonium in Salpeter- oder Salzsäurelösungen, welche ausserdem Fluorid enthalten, angewendet. Die Konzentration der beiden Säuren muss unter 3*N* liegen. Die Methode eignet sich auch für die Bestimmung von Zirkonium in Anwesenheit der folgenden Elemente: Uran, Titan, Niob, Tantal, Molybdän, Wolfram, Blei, Eisen, Kupfer und Zinn.

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CERATE OXIDIMETRY

IV. OXIDATION OF CARBOHYDRATES

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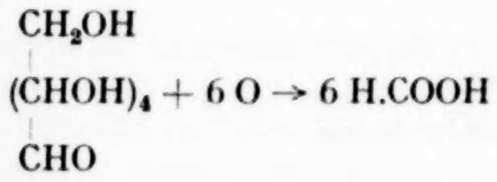
Several methods are available for the determination of reducing sugars including the classical Fehling and Benedict reagent methods, which are indirect and time-consuming. Another method, developed by WHITMOYER[1], involves the use of potassium ferricyanide. In this method, the reducing sugar is warmed with excess ferricyanide in sodium carbonate solution when an equivalent quantity of potassium ferrocyanide is produced. The solution is then acidified and the ferrocyanide titrated against standard ceric sulphate.

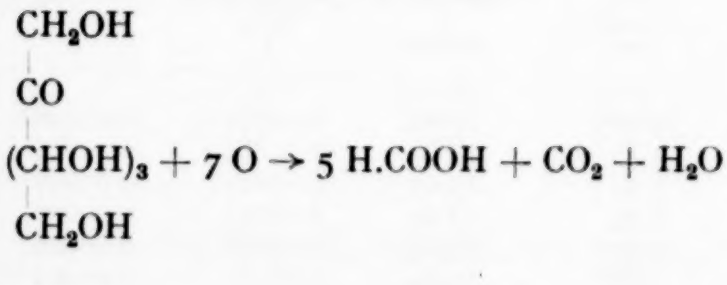
SMITH and co-workers[2] treated glucose with ceric perchlorate and found that it is oxidized to formic acid in 45 minutes, but the temperature of the reaction has to be controlled rather carefully.

Having studied the oxidizability of certain organic compounds with ceric sulphate[3,4,5], it was considered worth-while to study the action of ceric sulphate on reducing sugars. It has been found that the sugars containing the aldehydic group are oxidized to formic acid only:



$$\begin{array}{l} \mathrm{CH_2OH} \\ \mid \\ \mathrm{(CHOH)_4} + 6\,\mathrm{O} \rightarrow 6\,\mathrm{H.COOH} \\ \mid \\ \mathrm{CHO} \end{array}$$

In case of ketonic sugars also formic acid is the end-product but the ketonic group appears to be oxidized to carbon dioxide:



$$\begin{array}{l} \mathrm{CH_2OH} \\ \mid \\ \mathrm{CO} \\ \mid \\ \mathrm{(CHOH)_3} + 7\,\mathrm{O} \rightarrow 5\,\mathrm{H.COOH} + \mathrm{CO_2} + \mathrm{H_2O} \\ \mid \\ \mathrm{CH_2OH} \end{array}$$

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Disaccharides are first hydrolysed to ketonic and aldehydic sugars. These hydrolysed products can be estimated as above.

MATERIALS

Ceric sulphate was prepared from ceric ammonium nitrate (B.D.H. AnalaR). The ceric hydroxide was precipitated from an aqueous solution of ceric ammonium nitrate by ammonia. The precipitate was washed thoroughly (by decantation), filtered and left overnight under suction. It was then dissolved in 5*N* sulphuric acid. (It has, however, been observed that exactly the same results are obtained even with a ceric sulphate solution prepared by dissolving the ceric ammonium nitrate directly in sulphuric acid of required strength.)

All other chemicals employed were either B.D.H. AnalaR or Merck products.

EXPERIMENTAL

A standard solution of the sugar was prepared directly by weight. Known volumes of this solution were mixed with ceric sulphate and the mixture refluxed for different intervals of time, the remaining excess of the ceric sulphate being determined as described earlier[5]. The results obtained are given in the following tables.

Observations with glucose

TABLE I

Vol. of glucose soln. ml	*0.145N $Ce(SO_4)_2$ ml*	*Refluxing time min*	*$Ce(SO_4)_2$ consumed ml*	*Equivalents of O_2 consumed*	*Glucose found g*	*Glucose present g*
2	5	5	2.42	10.52	0.00527	0.00600
2	5	10	2.68	11.65	0.00583	0.00600
2	5	15	2.74	11.97	0.00597	0.00600
2	5	30	2.73	11.91	0.00595	0.00600
2	5	60	2.74	11.97	0.00597	0.00600
2	5	120	2.74	11.97	0.00597	0.00600
3	5	10	3.81	11.05	0.00829	0.00900
3	5	15	4.03	11.73	0.00877	0.00900
3	5	20	4.11	11.98	0.00895	0.00900

The above data show that glucose is oxidized to formic acid within 15 minutes if about 100% excess of ceric sulphate is present. However, the time required for complete reaction increases if the excess of ceric sulphate is less.

Observations with fructose

TABLE II

Vol. of fructose soln. ml	*0.145N $Ce(SO_4)_2$ ml*	*Refluxing time min*	*$Ce(SO_4)_2$ consumed ml*	*Equivalents of O_2 consumed*	*Fructose found g*	*Fructose present g*
2	5	10	3.065	12.82	0.00572	0.00626
2	5	15	3.355	14.04	0.00626	0.00626
2	5	30	3.34	13.97	0.00623	0.00626
2	5	60	3.34	13.97	0.00623	0.00626
2	5	120	3.355	14.04	0.00626	0.00626
1	5	10	1.666	13.94	0.00311	0.00313
1	5	15	1.676	14.02	0.00313	0.00313

Results in the Table II show that 14 equivalents of oxygen are consumed per mole of the fructose oxidized. Carbon dioxide was also detected as one of the reaction products. The reaction, therefore, appears to proceed as follows.

$$C_6H_{12}O_6 + 7\,O \rightarrow 5\,H.COOH + CO_2 + H_2O$$

Observations with sucrose

TABLE III

Vol. of sucrose soln. ml	*0.1275N $Ce(SO_4)_2$ ml*	*Refluxing time min*	*$Ce(SO_4)_2$ consumed ml*	*Equivalents of O_2 consumed*	*Sucrose found g*	*Sucrose present g*
2	5	5	2.49	24.70	0.00419	0.00442
2	5	10	2.61	25.89	0.00440	0.00442
2	5	15	2.61	25.89	0.00440	0.00442
2	5	30	2.60	25.80	0.00438	0.00442
2	5	60	2.61	25.89	0.00440	0.00442
2	5	135	2.61	25.89	0.00440	0.00442
3	5	10	2.51	16.50	0.00423	0.00663
3	5	20	3.69	24.41	0.00621	0.00663

Observations with lactose

TABLE IV

Vol. of lactose soln. ml	*0.1275N $Ce(SO_4)_2$ ml*	*Refluxing time min*	*$Ce(SO_4)_2$ consumed ml*	*Equivalents of O_2 consumed*	*Lactose found g*	*Lactose present g*
2	5	5	2.23	21.88	0.00375	0.00447
2	5	10	2.65	26.00	0.00446	0.00447
2	5	15	2.65	26.00	0.00446	0.00447
2	5	60	2.645	25.95	0.00445	0.00447
2	5	120	2.65	26.00	0.00446	0.00447
1	5	10	1.32	25.97	0.00222	0.00223
1	5	60	1.32	25.97	0.00222	0.00223
2	3	10	2.367	23.22	0.00398	0.00447
2	3	15	2.47	24.33	0.00416	0.00447

The data in Table III and IV show that in the presence of 100% excess of ceric sulphate, sucrose and lactose are both oxidized to formic acid according to the equation.

$$C_{12}H_{22}O_{11} + 13\,O \rightarrow 11\,H.COOH + CO_2$$

Observations with xylose

TABLE V

Vol. of xylose soln. ml	*0.1254N $Ce(SO_4)_2$ ml*	*Refluxing time min*	*$Ce(SO_4)_2$ consumed ml*	*Equivalents of O_2 consumed*	*Xylose found g*	*Xylose present g*
2	5	10	3.10	9.91	0.00584	0.00585
2	5	15	3.11	10.00	0.00585	0.00585
2	5	30	3.11	10.00	0.00585	0.00585
2	5	60	3.11	10.00	0.00585	0.00585

References p. 426.

The above table shows that xylose is oxidized to formic acid within 10 minutes

$$C_5H_{10}O_5 + 5\,O \rightarrow 5\,H.COOH$$

ACKNOWLEDGEMENT

My sincere thanks are to Dr. R. C. MEHROTRA, Reader in Chemistry, University of Lucknow, for his valuable guidance throughout the progress of this work.

SUMMARY

It has been shown that glucose and xylose are oxidized completely to formic acid with ceric sulphate and require respectively 12 and 10 equivalents of oxygen per gram mole of the sugar.

Under the same conditions, fructose requires 14 equivalents of oxygen per gram mole and in this case, the ketonic group is further oxidized to carbon dioxide.

The disaccharides can be estimated by the above procedure after hydrolysis.

RÉSUMÉ

Il est démontré que le glucose et le xylose peuvent être oxydés quantitativement en acide formique, au moyen de sulfate de cérium (IV), ce qui nécessite respectivement 12 et 10 équivalents d'oxygène par molécule-gramme de sucre.

Dans les mêmes conditions, le fructose exige 14 équivalents d'oxygène par molécule-gramme, et dans ce cas, le groupe cétonique est encore oxydé en anhydride carbonique.

Les disaccharides peuvent être dosés par le procédé décrit, après hydrolyse.

ZUSAMMENFASSUNG

Es wurde gezeigt, dass Glykose und Xylose durch Cer(IV)-sulfat vollständig zu Ameisensäure oxydiert werden. Für 1 Grammol der beiden aufgeführten Zucker werden 12 respektive 10 Äquivalente Sauerstoff gebraucht.

Unter den gleichen Bedingungen verbraucht Fruktose 14 Äquivalente Sauerstoff pro Grammol. In diesem Falle wird die Ketogruppe weiter zu Kohlendioxyd oxydiert.

Disaccharide können nach erfolgter Hydrolyse nach dem beschriebenen Verfahren bestimmt werden.

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5 : 6-BENZOQUINALDINIC ACID AS AN ANALYTICAL REAGENT
II. DETERMINATION OF TITANIUM

by

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In a previous communication[1] it was shown that the reagent 5:6-benzoquinaldinic acid could be used for the separation and determination of quite a large number of elements. This paper deals with the use of the reagent for the estimation of titanium and its separation from rare earths, alkaline earths, magnesium, thorium, zirconium and iron.

Titanium in the tetravalent state is completely precipitated at and above pH 3.0 and its separation from rare earths has been effected at a pH between 3.0 and 5.0. Ammonium salts help to keep the alkaline earths and magnesium in solution. The titanium complex with the reagent is never found to be of definite composition and hence, before weighing, it is ignited to the oxide.

PŘIBIL and his co-workers[2] separated titanium(IV) from iron(III) and aluminium by precipitation as hydroxide in presence of the disodium salt of ethylenediaminetetraacetic acid (complexone III). PICKERING[3] observed that the precipitation of titanium as the hydroxide in the presence of complexone was a slow process and so used a magnesium salt as a demasking agent for the quick and effective separation of small quantities of titanium.

Complexone forms a much more stable complex with magnesium than with titanium, which again forms a 5:6-benzoquinaldinic acid complex much less soluble than the magnesium benzoquinaldinate. The magnesium salt then acting as a demasking agent assists in the precipitation of titanium by the reagent in the presence of complexone. If the procedure is carried out with sufficient ammonium salt in solution to prevent precipitation of the magnesium, a good separation from thorium, zirconium and iron(III) can be readily accomplished. Aluminium is partially coprecipitated with the titanium during separation.

EXPERIMENTAL

Reagents and apparatus

Standard titanium solution was prepared from potassium titanium oxalate which was fumed with concentrated sulphuric acid containing ammonium sulphate. The solution was diluted and the titanium content standardized gravimetrically as the oxide.

A 1% alcoholic solution of 5 : 6-benzoquinaldinic acid, crystallized from glacial acetic acid and of m.p. 187° C, was used as the precipitant. All other chemicals used were of reagent quality.

Standard solutions used were prepared from reagent grade chemicals and their strengths were determined gravimetrically excepting that of calcium which was determined volumetrically.

A Cambridge bench model pH-meter was used for measurements of pH.

Procedure

Determination of titanium. The solution of titanium (TiO_2 = 27.6 mg) was diluted to 250 ml and to it was added a slight excess of the reagent. After heating the solution to boiling the pH was brought to the required value by dropwise addition of 2*N* ammonium hydroxide solution. The solution was left on a hot plate for 20-30 minutes and filtered, washed with hot 1% ammonium nitrate solution, dried and then ignited to TiO_2 before weighing (see Table I).

TABLE I

pH	*TiO_2 found* *mg*	*Error* *mg*
4.0	27.7	+0.1
3.5	27.6	0.0
3.0	27.7	+0.1
2.7	27.4	−0.2
2.5	27.0	−0.6

Separation from alkaline earths, rare earths and magnesium. Separation from rare earths, alkaline earths and magnesium was carried out by the procedure given above. The acidity was controlled by methyl orange, screened with indigo carmine, so that the pH was about 4 at the time of precipitation and the presence of ammonium chloride (5 g) helped to keep the magnesium and the alkaline earths in solution (see Table II).

TABLE II

Ions present *mg*	*pH*	*TiO_2 found* *mg*	*Error* *mg*
Mg^{+2} −100	4.0	27.5	−0.1
,, −100	4.0	27.6	0.0
Ca^{+2} −100	4.1	27.7	+0.1
,, −100	4.0	27.5	−0.1
Sr^{+2} −100	4.05	27.6	0.0
,, −100	4.0	27.5	−0.1
Ba^{+2} −100	4.2	27.8	+0.2
,, −100	4.0	27.5	−0.1
R_2O_3 −100	4.0	27.7	+0.1
,, −200	4.5	27.6	0.0
,, −200	4.8	27.5	−0.1

Determination in the presence of thorium, zirconium or iron(III). The acid titanium solution containing thorium, zirconium or iron was treated in succession with about 10 g of ammonium chloride, a few ml of 10% complexone III solution, a few ml of magnesium sulphate (10 g of $MgSO_4 \cdot 7H_2O$ in 100 ml) solution, sufficient reagent solution for complete precipitation of the titanium, and a few drops of screened methyl orange, and was finally diluted to 250 ml. The solution was brought to the boil and treated with 2*N* ammonium hydroxide until the colour of the indicator just changed to green. The solution was kept on a hot plate for about fifteen minutes, filtered, washed with hot 1% ammonium nitrate solution, ignited and weighed as TiO_2 (see Table III).

The amount of complexone added depended on the quantity of the other elements present and that of magnesium sulphate on the amount of excess complexone present in solution. Large excess of magnesium sulphate should be avoided as it affected the results for titanium separations from iron.

Separation from aluminium was not possible as it coprecipitated with titanium.

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TABLE III

Foreign element present *mg*	*10% Complexone* *ml*	*10% Magnesium sulphate* *ml*	*TiO_2 found* *mg*	*Error* *mg*
ZrO_2 — 26.5	5	10	27.5	−0.1
,, — 53	10	15	27.6	0.0
ThO_2 — 55.2	5	10	27.7	+0.1
,, —100.4	10	15	27.5	−0.1
Fe^{+3} — 25	10	15	27.7	+0.1
,, —100	20	20	27.5	−0.1
Al_2O_3 — 25	10	15	37.2	+9.6

Further work on the determination and separation of other elements is in progress.

SUMMARY

The reagent 5 : 6-benzoquinaldinic acid precipitates titanium(IV) completely from solution at and above pH 3.0 in the presence of rare earths. Coprecipitation of magnesium and the alkaline earths is easily prevented by the addition of ammonium chloride. Separation from iron(III), thorium or zirconium can be carried out in the presence of complexone III, magnesium sulphate being used as a demasking agent. Separation from aluminium is not possible. The titanium precipitate is not of definite composition and so it is ignited to the oxide before weighing.

RÉSUMÉ

L'acide 5 : 6-benzoquinaldinique précipite quantitativement le titane(IV) en solution de pH 3 ou de pH plus grand, en présence des éléments des terres rares. La coprécipitation du magnésium et des éléments alcalino-terreux est facilement empêchée par addition de chlorure d'ammonium. La séparation du fer(III), du thorium et du zirconium peut s'effectuer au moyen du complexon III, le sulfate de magnésium étant ensuite utilisé comme réactif de ,,démasquage". La séparation de l'aluminium n'est pas possible. Le précipité de titane obtenu doit être calciné en oxyde avant la pesée, sa composition étant mal définie.

ZUSAMMENFASSUNG

Die 5 : 6-Benzochinaldinsäure fällt das Titan(IV) in einer Lösung von pH 3 oder höher in Gegenwart der seltenen Erden quantitativ aus. Die Kopräzipitation von Magnesium und der Erdalkalien kann durch Zugabe von Ammoniumchlorid leicht verhindert werden. Die Abtrennung von Eisen(III), Thorium und Zirkonium kann mittels Komplexon III ausgeführt werden. Das Magnesiumsulfat wird darauf als demaskierendes Reagenz gebraucht. Die Abtrennung vom Aluminium ist nicht möglich. Der erhaltene Titan-Niederschlag muss, bevor er gewogen wird, zum Oxyd kalziniert werden, da er nicht einheitlich ist.

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CONTRIBUTION AU DOSAGE CHIMIQUE DES MATIÈRES PLOMBIFÈRES

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INTRODUCTION

Dans le contrôle de certaines opérations métallurgiques importantes, il est utile et même souvent nécessaire de connaître les teneurs des produits en les principaux composés plombifères (oxyde de plomb, sulfate de plomb, sulfure de plomb, peroxyde de plomb, plomb métallique, silicate de plomb). Actuellement, les ,,méthodes'' chimiques employées sont en fait des déterminations indirectes, obtenues généralement par différence à la suite de plusieurs dosages préalables. Il en résulte que les erreurs s'accumulent et que les résultats ne sont pas contrôlables.

Dans le but d'améliorer le contrôle de ces opérations, nous avons entrepris une étude détaillée du comportement chimique des composés plombifères normalement présents dans les minerais et les produits résultant du grillage de ces minerais. Nos essais ont tout d'abord porté sur les principaux composés, soit l'oxyde de plomb, le sulfure de plomb et le sulfate de plomb.

I. ÉTUDE DE L'OXYDE DE PLOMB, DU SULFURE DE PLOMB ET DU SULFATE DE PLOMB

A. POSITION DU PROBLÈME

Une méthode de dosage de l'oxyde de plomb, du sulfure de plomb et du sulfate de plomb est due à E. KROSSIN[1].

Sur trois prises différentes du produit à analyser, il détermine respectivement le plomb total, la somme (oxyde de plomb + sulfate de plomb) et l'oxyde de plomb. Pour cette dernière détermination l'oxyde de plomb contenu dans la matière à analyser est dissous sélectivement, mais le plomb n'est pas dosé dans la solution obtenue; seul est déterminé le plomb restant dans le résidu. La publication de E. KROSSIN n'expose que le principe des réactions sans préciser les détails opératoires.

Dans la méthode de KROSSIN, aucun composé n'est dosé par détermination directe et les teneurs en oxyde, sulfate et sulfate de plomb sont établies par *différences*. L'inconvénient majeur d'une telle méthode d'analyse est la proscription de toute vérification par un bilan; une erreur commise au cours d'une détermination influence

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tous les résultats obtenus. En outre, la multiplication des prises d'essai diminue la précision de l'échantillonnage.

Il est donc utile de trouver une méthode permettant d'effectuer le dosage *direct* de chacun des composés.

B. ACTION DE L'ACÉTATE D'AMMONIUM

1. *Essais de dissolution*

L'acétate d'ammonium est un des réactifs les plus employés dans l'analyse chimique quantitative des matières plombifères. Il convient donc de commencer les recherches par l'étude de ce réactif.

Chaque échantillon à étudier est finement broyé (100 % de passé à 200 mesh soit une dimension de particule inférieure à 74 microns), séché et attaqué pendant 30 minutes par une solution chaude d'acétate d'ammonium à 50% (un poids d'acétate pour un poids d'eau distillée). La lixiviation, qui se fait avec agitation modérée, niveau constant, et ébullition constante, donne un filtrat et un résidu. Dans le filtrat chaud, on ajoute une solution d'acide sulfurique à 20% (un volume d'acide sulfurique concentré pour quatre volumes d'eau distillée) et on précipite ainsi le plomb sous forme de sulfate. Celui-ci est filtré, lavé, calciné et pesé.

Le résidu est redissous dans l'eau régale. La solution est évaporée et traitée par l'acide sulfurique et l'acétate d'ammonium et le plomb est déterminé par la gravimétrie du sulfate.

Avant de faire confiance aux poids de plomb dosés dans le filtrat et le résidu d'une lixiviation, il faut vérifier si leur somme permet de retrouver le plomb total contenu dans l'échantillon soumis à l'attaque.

Au cours de ces essais de dissolution, il faut également s'assurer que l'opération a effectivement dissous tout ce qui est soluble. Dans ce but, il suffit d'effectuer plusieurs attaques successives en renouvelant le réactif jusqu'à ce qu'une dernière attaque ne dissolve plus rien. Cette vérification finale doit être appliquée à chacun des essais de lixiviation exposés ci-dessous.

Dans ces conditions opératoires, sont entièrement solubles dans l'acétate d'ammonium, l'oxyde et le sulfate tandis que le sulfure de plomb est complètement insoluble.

2. *Dosage sélectif du plomb par la gravimétrie du sulfate*

Comme on vient de l'exposer, les composés de plomb dissous dans l'acétate d'ammonium sont donc précipités par l'acide sulfurique et dosés par la gravimétrie du sulfate. A première vue, le résultat peut être faussé par les composés solubles de calcium, de strontium et de baryum qui accompagnent le plomb dans la précipitation par l'acide sulfurique. (Ces composés solubles dans l'acétate d'ammonium sont notamment, nous l'avons vérifié, les oxydes de Ca, Sr, Ba et le $CaSO_4$.) Nous avons constaté, par de nombreux déboires au cours des analyses, que ces éléments sont particulièrement gênants pour des solutions froides, riches en acide et riches en sels d'ammonium. Une étude des conditions de précipitation des sels de Pb, Ca, Ba, Sr et NH_4 nous a permis de déterminer des conditions opératoires dans lesquelles le sulfate de plomb est précipité sélectivement.

Dans ce procédé, les produits de l'attaque par l'acétate d'ammonium sont filtrés à chaud et la précipitation du plomb se fait alors en versant dans ce filtrat une solution chaude d'acide sulfurique à 20% (un volume d'acide sulfurique concentré pour quatre volumes d'eau distillée). L'addition d'un peu d'alcool méthylique après la réaction (acide sulfurique + solution d'acétate) permet de vérifier si la précipitation du plomb est complète.

La vérification de la présence de sels de Ca, Sr et Ba dans le nouveau filtrat a été faite, après refroidissement, par l'acide sulfurique ou l'oxalate d'ammonium. La présence de sels d'ammonium est également mise en relief par une ébullition suivie d'un refroidissement rapide.

Cette méthode assure la précipitation sélective du sulfate de plomb et présente

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également l'avantage de diminuer le temps nécessaire à la formation d'un précipité séparable facilement par filtration. Appliquée chaque fois avant la filtration terminale du plomb, elle permet d'éliminer l'influence pertubatrice des alcalinoterreux.

C. ACTION DE L'ACIDE RICINOLÉIQUE

1. *Aspect de la recherche*

L'acide ricinoléique est le réactif utilisé par E. KROSSIN. Comme cet auteur ne donne pas de détails dans son article, nous avons dû élaborer le mode opératoire en surmontant de nombreuses difficultés. Nous exposons tout d'abord la méthode qui nous a permis de vérifier la conclusion de KROSSIN relative à la dissolution sélective de l'oxyde de plomb dans l'acide ricinoléique.

2. *Principe des opérations*

Le minerai est attaqué par de l'acide ricinoléique pur puis de l'alcool méthylique à une température voisine de 40° C. Après filtration sur un entonnoir chauffé, on obtient un résidu et un filtrat.

Le résidu est redissous par l'eau régale, puis précipité par l'acide sulfurique à l'état de sulfate de plomb. Ce sulfate est lavé, séché, calciné et pesé. Le filtrat est très difficile à analyser. Après avoir essayé un grand nombre de procédés, nous avons adopté la méthode suivante: élimination de l'alcool par évaporation, précipitation de l'acide sulfhydrique, reprise par acide nitrique et acide sulfurique et pesée à l'état de sulfate de plomb.

3. *Détails du mode opératoire*

On verse dans un vase de Berlin de 400 ml, forme basse, 50 g d'acide ricinoléique pur que l'on porte au bain-marie jusqu'à ce que l'acide ricinoléique soit bien limpide. A ce moment on ajoute petit à petit, tout en agitant constamment, une prise d'essai d'échantillon de 2 g. On laisse digérer pendant 4 heures en agitant de temps en temps. Vers la fin de cette opération, on chauffe de l'alcool méthylique le plus pur possible à une température voisine de 40° C. Au bout des 4 heures on laisse refroidir le mélange acide ricinoléique-composés plombifères pendant quelques minutes de telle façon qu'il ne prenne pas en masse, puis on ajoute 50 ml d'alcool méthylique pur et le reporte au bain-marie. Lorsque la solution est limpide, c'est-à-dire après une dizaine de minutes, on filtre sur un entonnoir chauffé. Cet entonnoir est chauffé, pendant toute la filtration, dans un dispositif analogue à un bain-marie dont on aurait enlevé une partie du fond. La filtration terminée, on lave le vase d'attaque à l'alcool chaud puis on filtre et lave jusqu'à élimination complète de la matière grasse. On obtient d'une part un résidu et d'autre part un filtrat.

4. *Analyse du résidu*

Le résidu est repris par 50 ml d'eau régale, puis évaporé presque à sec, repris par 20 ml d'acide sulfurique 50%. On évapore jusqu'à fumées blanches, reprend par l'eau, porte à l'ébullition pendant une dizaine de minutes et on laisse reposer pendant 12 heures. Après filtration, le précipité est lavé par l'acide sulfurique, puis à l'alcool pour éliminer les dernières traces d'acide sulfurique. Enfin, le précipité est séché à l'étuve à 100 pendant 3 heures, calciné à 550° pendant 45 minutes et pesé.

5. *Analyse du filtrat*

La solution alcoolique, contenant des composés gras, est assez difficile à analyser et c'est peut-être à cause de cette difficulté que E. KROSSIN dosait le plomb uniquement dans les résidus de lixiviations.

Après l'essai de plusieurs procédés, dont la saponification et l'électrolyse en milieu basique, nous avons adopté une méthode basée sur la précipitation par l'acide sulfhydrique et gravimétrie du sulfate.

Dans cette méthode, on chauffe le filtrat pour éliminer l'alcool, puis on y verse de l'hydroxyde de sodium en excès et on sature le milieu en H_2S. Après une décantation de trois heures, le résidu est repris par l'acide nitrique, puis par l'acide sulfurique et traité par la méthode de dosage gravimétrique du sulfate.

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6. *Amélioration de la méthode*

La méthode qui vient d'être décrite présente quelques inconvénients de détail. En particulier, elle rend difficile le maintien de la température au cours de la lixiviation et donne lieu à des difficultés au cours de la filtration. Elle a été améliorée au cours des recherches. Ainsi les conditions de la lixiviation ont été modifiées en s'inspirant de la méthode qui venait d'être mise au point pour les composés zincifères[2].

L'échantillon est attaqué à chaud par un mélange d'alcool méthylique et d'acide ricinoléique. L'erlenmeyer contenant le mélange est surmonté d'un réfrigérant de Liebig et l'alcool condensé retombe dans le vase. La température est ainsi maintenue automatiquement aux environs de 66° C. Le remplacement de l'alcool méthylique par de l'alcool éthylique permet de travailler à 78° C.

Les détails sont exposés plus loin dans la méthode d'analyse moléculaire.

D. L'ANALYSE DE L'OXYDE DE PLOMB, DU SULFATE DE PLOMB ET DU SULFURE DE PLOMB

Les lixiviations des matières plombifères ont donc permis de dissoudre de manière sélective, d'une part l'oxyde de plomb dans l'acide ricinoléique et d'autre part le sulfate de plomb et l'oxyde de plomb dans l'acétate d'ammonium. Par ailleurs, il est bien connu, et nous l'avons vérifié une fois de plus, que le sulfure de plomb est complètement soluble dans l'acide nitrique.

Il ressort de ces essais un résultat pratique important: la possibilité de faire l'analyse moléculaire exacte d'un produit dans lequel les composés plombifères se réduisent à l'oxyde, le sulfate et le sulfure (cas fréquent dans la pratique).

Le Tableau I expose le schéma de la méthode proposée.

E. DESCRIPTION SUCCINCTE DU MODE OPÉRATOIRE

Prise d'essai: 5 g (poids sec) broyé à 200 mesh.

1. *Lixiviation dans l'acide ricinoléique*

La prise d'essai est introduite dans un petit erlenmeyer de 200 à 250 ml. Ajouter 10 ml d'alcool méthylique, agiter, puis ajouter 75 g d'acide ricinoléique chaud (60° C environ) et agiterdenouveau. Adapter alors à l'erlenmeyer un réfrigérant Liebig et chauffer l'erlenmeyer, avec précaution au début, jusqu'à l'ébullition. Les vapeurs d'alcool, condensées, retombent dans le vase et maintiennent la constance de la température.

A la fin de l'attaque, laisser refroidir quelque peu, enlever le réfrigérant Liebig, ajouter 100 ml d'alcool chaud et porter au bain-marie à une température d'environ 60° C pendant une dizaine de minutes (ne pas trop dépasser ce temps sinon l'alcool s'évapore et le milieu devient difficile à filtrer). La filtration se fait sur filtre chauffé au moyen d'un entonnoir plongeant dans un bain-marie dont le fond est perforé pour laisser passer la tige de l'entonnoir. Laver à l'alcool chaud.

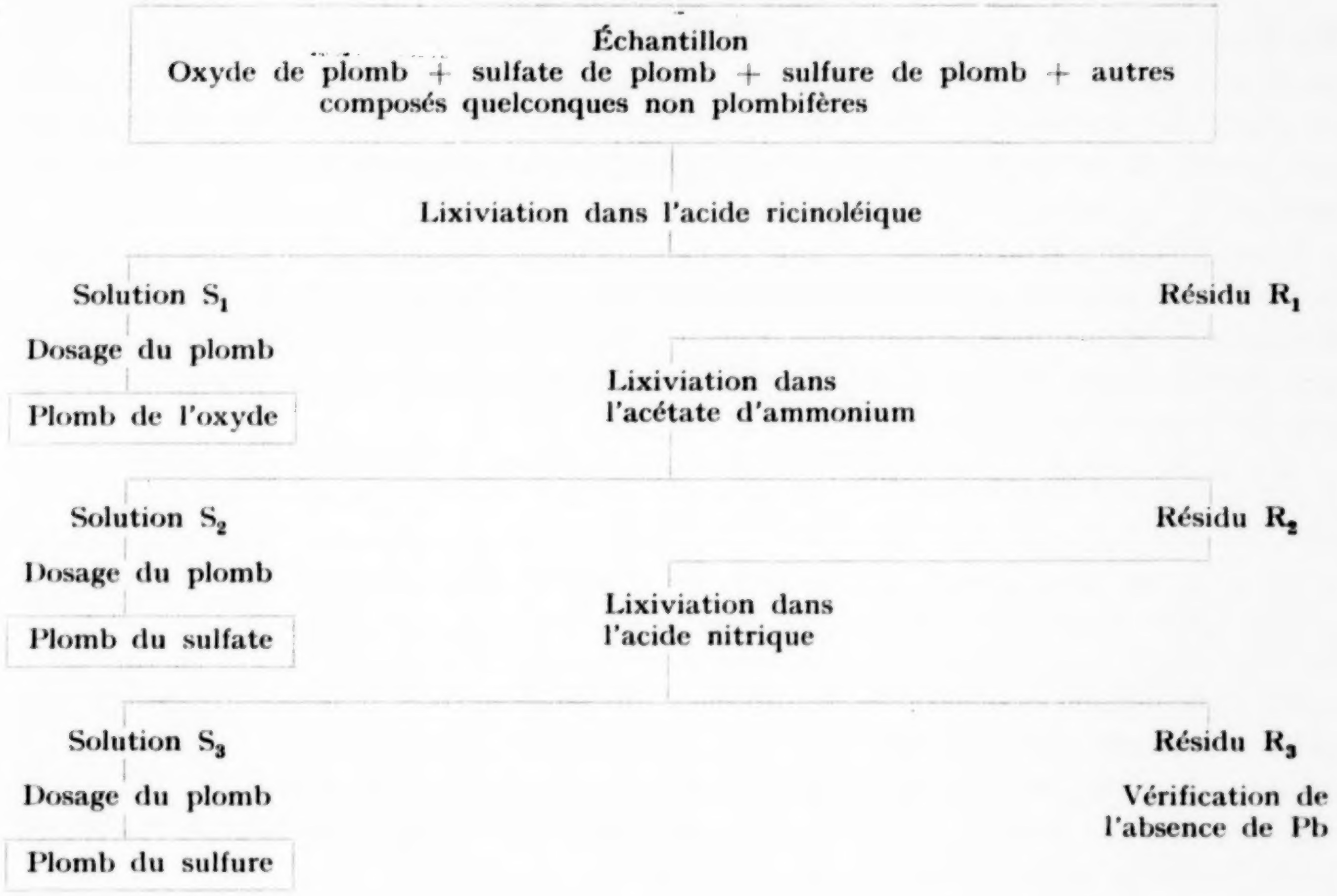
La durée de l'attaque est variable. En général dans nos essais, la première attaque durait 8 heures et était suivie d'attaque de 2 heures jusqu'à constatation de l'absence de plomb dans le filtrat de la dernière attaque. Une attaque de 8 heures et deux attaques de 2 heures suffisaient dans la plupart des cas.

Lorsque les produits à analyser sont réputés particulièrement riches en composés plombifères, on peut éventuellement partir d'une prise d'essai de 2 g (au lieu de 5 g) dans le but de diminuer le nombre d'attaques.

La filtration sépare la solution S_1 du résidu R_1.

TABLEAU I

SCHÉMA DE LA MÉTHODE


Échantillon
Oxyde de plomb + sulfate de plomb + sulfure de plomb + autres composés quelconques non plombifères
Lixiviation dans l'acide ricinoléique
Solution S_1
Résidu R_1
Dosage du plomb
Plomb de l'oxyde
Lixiviation dans l'acétate d'ammonium
Solution S_2
Résidu R_2
Dosage du plomb
Plomb du sulfate
Lixiviation dans l'acide nitrique
Solution S_3
Résidu R_3
Dosage du plomb
Plomb du sulfure
Vérification de l'absence de Pb

Analyse de vérification: dosage direct du plomb total dans l'échantillon initial

2. *Détermination de l'oxyde de plomb*

La solution S_1 est chauffée pour éliminer l'alcool. Celui-ci étant éliminé et le milieu étant limpide, ajouter une solution concentrée d'hydroxyde de sodium en excès puis faire passer l'acide sulfhydrique jusqu'à saturation et laisser décanter trois heures. Filtrer et vérifier l'absence du plomb dans le filtrat. Trouer le filtre et à l'aide d'un peu d'eau chaude (pissette), faire tomber la majeure partie du précipité dans un vase propre placé sous l'entonnoir. Reprendre alors le résidu restant sur le filtre par 150 ml d'acide nitrique à 50% avec addition de quelques gouttes de brome. Faire bouillir le tout jusqu'à réduction du volume liquide à environ 100 ml. Laisser refroidir jusqu'à moins de 30° C, ajouter 200 ml d'acide sulfurique 50% et évaporer jusqu'à fumées blanches. Reprendre par l'eau chaude (appliquer éventuellement le procédé de précipitation sélective du plomb exposé plus haut) et laisser reposer jusqu'à obtention d'un précipité bien décanté et bien grenu.

Le précipité de sulfate de plomb est filtré, lavé à l'eau chargée d'acide sulfurique (5 %), lavé à l'eau chaude puis à l'alcool éthylique (vérifier l'absence de plomb dans le filtrat). Le précipité est ensuite séché, calciné à 550° C pendant une heure et pesé. Le poids de plomb obtenu représente l'oxyde de plomb présent dans l'échantillon analysé.

Signalons ici que, au cours du lavage final du sulfate de plomb, l'alcool éthylique permet d'obtenir des résultats plus précis que ceux obtenus avec l'alcool méthylique.

3. *Lixiviation dans l'acétate d'ammonium*

Le résidu R_1 est attaqué par 250 ml d'une solution d'acétate d'ammonium à 50 %. La lixiviation se fait à chaud et l'ébullition est prolongée pendant une demi-heure. Le niveau du liquide est maintenu constant au moyen d'eau distillée dans le but de conserver la même concentration en acétate. Répéter éventuellement l'attaque jusqu'à dissolution complète du composé plombifère soluble (en général deux attaques suffisent). La filtration se fait à chaud et donne un résidu R_2 (lavé à l'eau chaude) et une solution S_2.

4. *Détermination du sulfate de plomb*

La solution S_2 est tout d'abord étendue par 300 ml d'eau chaude et portée à une température voisine de 80° C. Pendant ce temps, préparer une solution d'acide sulfurique à 20 % et chauffer cette solution également à 80° C (niveau constant). Verser lentement 100 ml de la solution sulfurique chaude dans la solution d'acétate. Laisser déposer le mélange à une température voisine de 40° C jusqu'à obtention d'un précipité bien décanté et bien grenu (2 à 3 heures). Filtrer la pulpe chaude, laver à l'eau sulfurique 5%, à l'eau chaude, puis à l'alcool éthylique (vérifier l'absence de plomb dans le filtrat). Sécher le précipité, calciner une heure à 550° C et peser.

Le poids de plomb obtenu représente le sulfate de plomb présent dans l'échantillon analysé.

5. *Détermination du sulfure de plomb*

Le résidu R_2 est attaqué par 50 ml d'acide nitrique 50 % avec addition de quelques gouttes de brome. La solution est évaporée et reprise par de l'eau chaude. Laisser refroidir un peu, ajouter 100 ml d'acide sulfurique 50 % et évaporer jusqu'à fumées blanches. Reprendre par l'eau chaude (appliquer éventuellement le procédé de séparation sélective du sulfate de plomb) et laisser déposer jusqu'à obtention d'un précipité bien décanté et bien grenu. Filtrer, laver à l'eau chaude sulfurique 5 %, à l'eau chaude et à l'alcool éthylique, sécher, calciner une heure à 550° C et peser. Le poids de plomb obtenu représente le sulfure de plomb présent dans l'échantillon.

La somme des teneurs en oxyde de plomb, en sulfate de plomb et en sulfure de plomb doit correspondre à la teneur de l'échantillon en plomb total.

F. CONCLUSIONS

La méthode proposée permet des séparations sélectives et constitue une amélioration du procédé préconisé par E. KROSSIN dans son article.

En effet,

1) Elle ne comporte aucun résultat établi par différence.
2) C'est une méthode continue d'opérations successives sur le même échantillon de départ.
3) Elle réduit le temps consacré à la préparation des échantillons (qui doivent être finement broyés) et augmente la précision de l'échantillonnage.
4) Elle utilise chaque produit des lixiviations jusqu'au résidu final où l'absence de plomb est vérifiée.
5) Elle assure le contrôle des résultats par des bilans exacts.

II. ÉTUDE DU SILICATE DE PLOMB, DU PEROXYDE DE PLOMB ET DU PLOMB MÉTALLIQUE

A. POSITION DU PROBLÈME

En ce qui concerne l'analyse des silicate, peroxyde et plomb métallique, nous n'avons trouvé aucune méthode susceptible d'orienter les recherches. Il a donc bien fallu se livrer à des investigations par tâtonnements sur l'action de plusieurs réactifs, et étudier plus en détail les réactifs donnant des résultats intéressants.

Il convient tout d'abord d'étudier l'action de l'acide ricinoléique et de l'acétate d'ammonium. Les essais montrent que le silicate est soluble tandis que le métal et le peroxyde sont insolubles. Le silicate accompagne donc l'oxyde au cours de l'analyse moléculaire.

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B. ACTION DE L'ACIDE CHLORHYDRIQUE

Dans ces essais, l'échantillon est lixivié dans l'acide chlorhydrique. Le filtrat est traité par l'acide sulfurique 20% et la gravimétrie du sulfate tandis que le résidu est redissous dans l'acide nitrique puis également traité par la gravimétrie du sulfate. Dans ces essais, nous avons fait varier la température de la lixiviation et la concentration de l'acide chlorhydrique. Des essais systématiques établissent que le peroxyde est complètement soluble dans l'acide chlorhydrique dilué froid tandis que le sulfure et le métal restent insolubles.

C. ACTION DU PERHYDROL

Les échantillons de sulfure et de plomb métallique sont lixiviés dans une solution de perhydrol. Après une filtration qui élimine l'excès d'eau oxygénée, le résidu est lavé et attaqué par une solution chaude d'acétate d'ammonium. Les filtrat et résidu de cette opération sont traités comme il est indiqué plus haut au cours de l'exposé relatif à l'action de l'acétate d'ammonium. Le perhydrol doit être rigoureusement exempt d'acides.

Les essais de dissolution ont montré qu'après ce double traitement le sulfure est complètement soluble tandis que le plomb métal est insoluble.

Le procédé présente néanmoins l'inconvénient de donner lieu à une réaction très violente au début de la lixiviation par le perhydrol. En conséquence nous avons modifié le mode opératoire en commençant les attaques par une solution diluée en perhydrol pour terminer par une lixiviation dans le perhydrol pur.

D. MÉTHODE D'ANALYSE MOLÉCULAIRE

En possession de ces données, nous avons complété la méthode donnée dans le Tableau I par celle représentée par le Tableau II.

Cette méthode s'est révélée très satisfaisante dans son application à des mélanges synthétiques obtenus en partant de produits réputés purs.

1. L'échantillon est tout d'abord traité par l'acide ricinoléique et l'acétate d'ammonium, comme il a été exposé en détail ci-dessus. On obtient de cette manière l'oxyde de plomb, le silicate de plomb, et le sulfate de plomb.
2. Le résidu R_2 résultant de l'attaque par l'acétate d'ammonium lixivié dans 500 ml d'une solution d'acide chlorhydrique avec agitation mécanique pendant deux heures (répéter éventuellement la lixiviation). La filtration sépare un résidu R_3 d'une solution S_3. Celle ci est évaporée puis traitée par l'acide sulfurique et la gravimétrie du sulfate comme nous l'avons déjà exposé. Le résultat du dosage correspond au peroxyde de plomb.
3. Le résidu R_3 est lixivié tout d'abord par 100 ml d'une solution de perhydrol à 10 % et ensuite par 100 ml de perhydrol pur. Après filtration, le produit est attaqué 30 minutes dans l'acétate d'ammonium chaud et le filtrat S_4 est traité par la gravimétrie du sulfate. On obtient ainsi le sulfure de plomb.
4. Le résidu R_4 subit le traitement à l'acide nitrique déjà décrit en détail dans la première partie de cette étude et le résultat représente le plomb métallique.

Il importe de vérifier l'absence de plomb dans le résidu final non attaqué par l'acide nitrique.

La méthode a été appliquée à des produits chauffés à diverses températures puis refroidis. Les résultats ont montré que la sélectivité des réactifs n'est pas affec-

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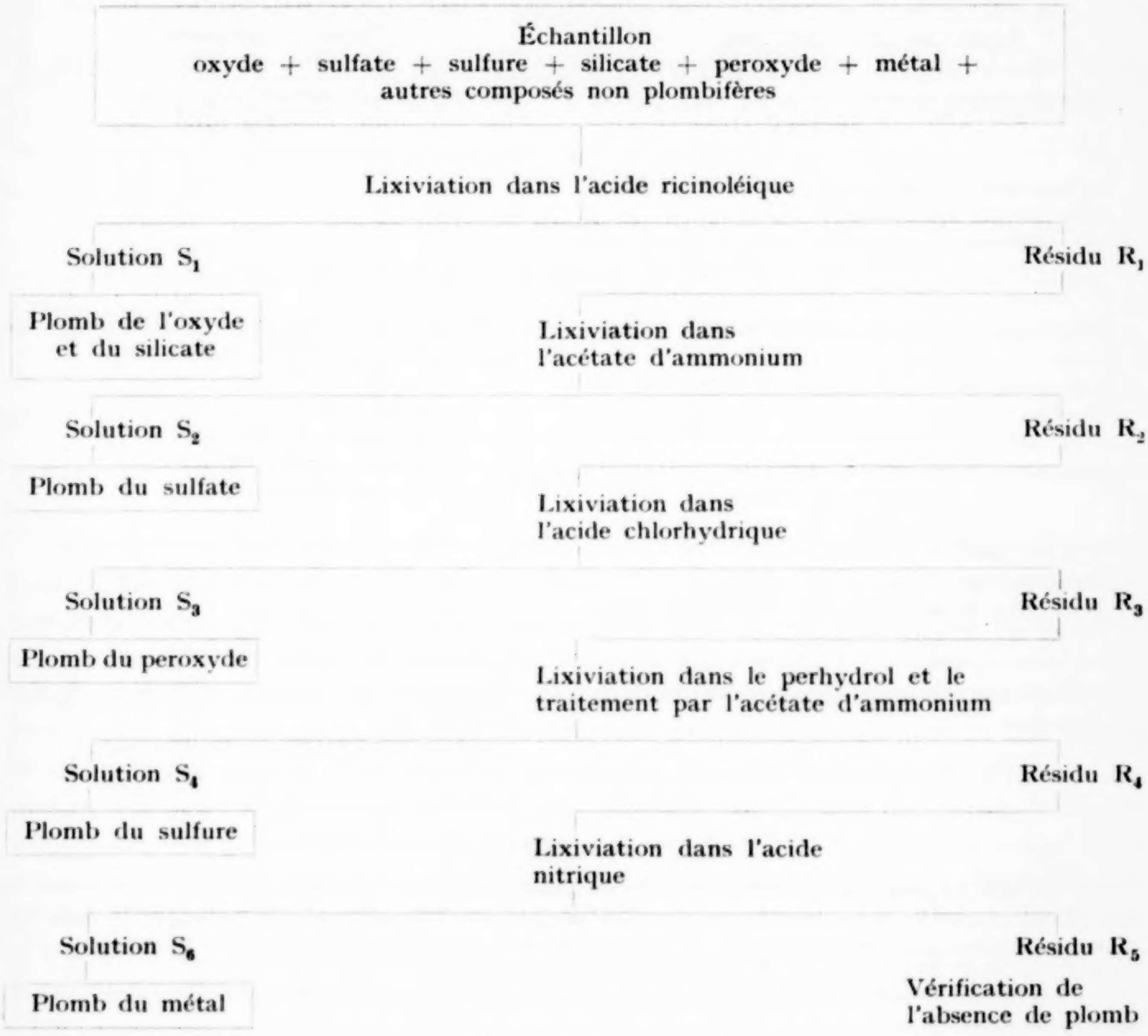
TABLEAU II

SCHÉMA DE PRINCIPE DE L'ANALYSE MOLÉCULAIRE


Échantillon
oxyde + sulfate + sulfure + silicate + peroxyde + métal + autres composés non plombifères
Lixiviation dans l'acide ricinoléique
Solution S_1
Résidu R_1
Plomb de l'oxyde et du silicate
Lixiviation dans l'acétate d'ammonium
Solution S_2
Résidu R_2
Plomb du sulfate
Lixiviation dans l'acide chlorhydrique
Solution S_3
Résidu R_3
Plomb du peroxyde
Lixiviation dans le perhydrol et le traitement par l'acétate d'ammonium
Solution S_4
Résidu R_4
Plomb du sulfure
Lixiviation dans l'acide nitrique
Solution S_6
Résidu R_5
Plomb du métal
Vérification de l'absence de plomb

Analyse de vérification: dosage direct du plomb total dans l'échantillon initial.

tée et que seule est modifiée la durée de dissolution dans les réactifs. En particulier, l'attaque de l'oxyde dans l'acide ricinoléique est plus lente lorsque l'oxyde a été chauffé puis refroidi au préalable et devient encore plus paresseuse lorsque le chauffage a été suivi d'un refroidissement rapide.

L'analyse moléculaire a été également appliquée avec succès à des minerais de galène, des produits grillés et supergrillés et des mattes plombifères. La méthode préconisée est comparée aux anciennes déterminations dans le Tableau III en ce qui concerne le dosage chimique de l'oxyde, du peroxyde, du métal, du sulfure et du sulfate.

Telle qu'elle se présente, cette méthode d'analyse moléculaire peut faciliter de manière appréciable l'étude des problèmes métallurgiques relatifs aux minerais et aux produits métallurgiques plombifères. Elle permet notamment le contrôle automatique des analyses en proscrivant tout résultat obtenu par différence.

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TABLEAU III

COMPARAISON ENTRE LES ANCIENNES DÉTERMINATIONS ET LA MÉTHODE PROPOSÉE

Anciennes déterminations	Méthode proposée
Détermination directe du Pb total (1)	Détermination directe du Pb total (1)
Détermination des composés non solubles dans l'acide ricinoléique. Par différence avec (1) on a l'oxyde de Pb (2)	
Détermination de la somme (oxyde + sulfate) Par différence avec (2) on a le sulfate de Pb (3)	Déterminations directes et sélectives, sur une seule prise d'échantillon, de oxyde de Pb (2) sulfate de Pb (3) peroxyde de Pb (4) sulfure de Pb (5) Pb métallique (6)
Aucune détermination sélective du peroxyde de Pb (4) du sulfure de Pb (5) du Pb métallique (6) Seule la somme (4) + (5) + (6) peut être déterminée par différence entre (1) et (2) + (3)	
Aucun contrôle systématique des résultats obtenus	La somme (2 + 3 + 4 + 5 + 6) doit donner (1) Contrôle automatique des résultats

RÉSUMÉ

Cet article expose une méthode d'analyse quantitative de différents composés moléculaires du plomb présents dans des minerais et des produits métallurgiques. En principe, la méthode consiste à dissoudre sélectivement et successivement les différents composés plombifères et à doser le plomb dans chacune des solutions obtenues.

La méthode permet le contrôle automatique des analyses en proscrivant tout résultat obtenu par différence.

SUMMARY

This paper describes a method for the quantitative determination of various lead compounds present in ores and metallurgical products. The method consists, in principle, of dissolving selectively and successively the different lead compounds and determining the lead in each of the filtrates thus obtained.

The method guarantees the automatic control of the results.

ZUSAMMENFASSUNG

Dieser Artikel stellt eine quantitative Methode für die verschiedenen sich in Erzen und metallurgischen Produkten befindenden Bleiverbindungen dar. Das Prinzip der Methode besteht daraus dass die verschiedenen Bleiverbindungen selektiv und nach einander aufgelöst werden und das Blei in jedem erhaltenen Filtrat bestimmt wird.

Die Methode gestattet die automatische Kontrolle der Analysen, unter Vermeidung jedes durch Differenz erzeugten Resultates.

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A QUICK AND PRECISE HETEROMETRIC DETERMINATION OF IRON WITH ALUMINON IN EXCESSES OF FOREIGN METALS

by

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INTRODUCTION

In a previous heterometric investigation the reaction of iron(III), chromium(III) and aluminium with aluminon was studied[1]. The existence of a series of compounds was established and their character was investigated. It was shown that in mixtures containing all three cations the insoluble compounds of iron were heterometrically formed quantitatively, *before* any reaction with chromium or aluminium occurred. It was found that this was even the case in solutions which contained only a few tenths of one percent of iron. The working conditions and the influence of other foreign metals which were present in solution were studied. In all cases the titration of iron with aluminon proceeded smoothly and the titration lasted 10-15 minutes. In a $0.000375M$ solution of iron (= 0.2 mg Fe) containing more than 99.5% foreign metal, the determination could generally be made with an error of 0-2%. When the amount of iron analysed was as high as 0.5 mg, the error was always equal to zero. No previous separations whatever were necessary. The method presented is applicable in all cases where the thiocyanate method is impossible. The *end-point* of the titration is obtained at the molar ratio of 1 iron: 3 aluminon (= $Fe(AN)_3\downarrow\downarrow$). It is very important that this point, derived from the curves, should be clear cut, should coincide with the *first* optical maximum density point and not change on further addition of titrant. It was ascertained that this was the case only with pure iron solutions. In the presence of other metals the maximum density values increased gradually and continuously with the further addition of titrant. Due to this the determination of the end-point became impossible. In contrast to the behaviour of other metals, *in the presence of chromium, a strictly horizontal line was obtained.*

It was found that the addition of a definite amount of a chromium salt was essential in all titrations in order to obtain a precise and safe *first* maximum optical density point. This addition of chromium was made when the iron was determined in excess of all other foreign metals tested.

EXPERIMENTAL

The same apparatus and the same technique were used as in previous heterometric investigations[2,3]. All titrations were made using a thick and deep red filter (Corning No. 2408). The

TABLE I

Composition: 9 ml aqueous solution + 1 ml *M* CH_3COOH + *x* ml m*M* aluminon (= AN).

Experiment number	*Solution*							*Molarity of AN (= m)*	*% of iron*
	$Fe(NO_3)_3$		*$Cr(NO_3)_3$*		*Salt*				
	ml	*molar*	*ml*	*molar*	*name*	*ml*	*molar*		
1	3	0.00125	—	—	—	—	—	0.00333	
2	3	0.00125	2	0.02	—	—	—	0.00333	
3	3	0.00125	2	0.1	—	—	—	0.00333	
4	3	0.00125	1	1.0	—	—	—	0.00333	0.4
5	3	0.00125	2	1.0	—	—	—	0.00333	0.2
6	3	0.00125	—	—	$Al(NO_3)_3$	1	0.1	0.00333	8
7	3	0.00125	—	—	,,	1	1.0	0.00333	0.8
8	3	0.00125	—	—	,,	1	3.0	0.00333	0.25
9	3	0.00125	1	1.0	,,	1	1.0	0.00333	0.4
10	3	0.00125	1	1.0	$Co(NO_3)_3$	1	1.0	0.00333	0.35
11	3	0.00125	1	1.0	$Cu(NO_3)_2$	1	1.0	0.00333	0.33
12	3	0.00125	1	1.0	$Ni(NO_3)_2$	1	1.0	0.00333	0.35
13	3	0.00125	1	1.0	$Pb(NO_3)_2$	1	1.0	0.00333	0.1
14	3	0.00125	1	1.0	$MnCl_2$	1	1.0	0.00333	0.37
15	4	0.00250	—	—	—	—	—	0.00666	—
16	4	0.00250	2	1.0	—	—	—	0.00666	0.53
17	4	0.00250	2	1.0	$Al(NO_3)_3$	2	1.0	0.00666	1.0
18	4	0.00250	2	1.0	$Co(NO_3)_2$	2	1.0	0.00666	0.47
19	4	0.00250	2	1.0	$Ni(NO_3)_2$	2	1.0	0.00666	0.47
20	4	0.00250	2	1.0	$Cu(NO_3)_2$	2	1.0	0.00666	0.43
21	4	0.00250	2	1.0	$Pb(NO_3)_2$	2	1.0	0.00666	0.13
22	4	0.00250	2	1.0	$Cd(NO_3)_2$	2	1.0	0.00666	0.25
23	4	0.00250	2	1.0	$MnCl_2$	2	1.0	0.00666	0.5
24	4	0.00250	2	1.0	$ZnCl_2$	2	1.0	0.00666	0.42
25	4	0.00250	2	1.0	$MgSO_4$	2	1.0	0.00666	1.1
26	4	0.00250	2	1.0	$Ba(NO_3)_2$	2	1.0	0.00666	0.2
27	4	0.00250	2	1.0	$Ca(NO_3)_2$	2	1.0	0.00666	0.7

c = contact point.

chemicals used were all AnalaR or chemically pure reagents. The aluminon used was a British Drug House reagent. The iron nitrate solutions were prepared from a molar stock solution of iron containing nitric acid at a concentration of two molar. The iron solution was diluted in steps in order to give the desired final molarity. Although the obtained dilute solutions contained free nitric acid they were freshly prepared for each series of titrations. In all titrations the analysed volume was made with water to equal 10 ml. A microburet of 5 ml volume (0.01 ml) was used, the reaction vessel was cylindrical and had a diameter of 4 cm. The temperature of the vessel was thermostatically controlled at 20° C. The aluminon was dissolved in water. Generally, the end-point of the titration was obtained from enlarged heterometric titration curves, by the intersection of two lines, the maximum density line and the line of the last quarter of the titration curve.

RESULTS AND DISCUSSION

General

Table 1 and Figs. 1-3 contain a small selection of the titrations made. The numbers are the same in the table and in the curves. The composition of each experiment may be read from the table. In the table the calculated percentage of iron in the mixture was made on the basis of the sum of the iron and foreign metals present, but the added chromium was not taken into account. Only when chromium was considered the foreign metal was the % of iron calculated in relation to the chromium.

Content iron: 0.2097 mg or 0.5592 mg. T = 20° C. Red filter Corning (No. 2408)

x ml AN calculated at:		*x ml AN found at:*		*Optical density at:*		*% error at:*	*Titration time in minutes*	*Remarks*
1:1	*1:3*	*1:1*	*1:3*	*1:1*	*1:3*	*1:3*		
1.13	3.38	1.0	3.46	0.31	0.42	+2.4	15	
		—	3.40	0.31	0.40	+0.6	15	Horizontal maximum line
		—	3.40	0.30	0.41	+0.6	10	,, ,, ,,
		—	3.40	0.18	0.34	+0.6	12	,, ,, ,,
		—	3.42	—	0.25	+1.2	15	Slightly increasing maximum line
		—	—	—	—	—	—	A continuously increasing optical density line without breaks.
		—	—	—	—	—	—	
		—	—	—	—	—	—	
		—	3.40	—	0.29	+0.6	15	Horizontal maximum line
		—	3.50	—	0.37	+3.6	10	,, ,, ,,
		—	3.45	—	0.32	+2.1	10	,, ,, ,,
		—	3.46	—	0.36	+2.3	10	,, ,, ,,
		—	3.45	—	0.33	+2.1	10	,, ,, ,,
		—	3.45	—	0.31	+2.1	10	,, ,, ,,
1.50	4.50	c 1.6	4.50	0.72	0.99	0.0	10	,, ,, ,,
		—	4.50	—	0.62	0.0	10	,, ,, ,,
		—	4.50	—	0.57	0.0	15	,, ,, ,,
		—	4.50	—	0.64	0.0	15	,, ,, ,,
		c 1.6	c 4.50	—	0.48	0.0	15	,, ,, ,,
		—	4.50	—	0.36	0.0	10	,, ,, ,,
		—	4.50	—	0.67	0.0	10	,, ,, ,,
		—	4.50	—	0.69	0.0	10	,, ,, ,,
		—	4.50	—	0.69	0.0	10	,, ,, ,,
		—	4.50	—	0.73	0.0	10	,, ,, ,,
		—	4.50	—	0.67	0.0	10	,, ,, ,,
		—	4.50	—	0.73	0.0	10	,, ,, ,,
		—	4.50	—	0.67	0.0	10	,, ,, ,,

In all cases (with the exception of expts. 6-8) *horizontal* maximum density lines were obtained at the end of the titration.

Many titrations of iron were carried out in the presence of excesses of bivalent cations; but in the absence of chromium, in no case was a horizontal maximum line obtained. The density values continued to increase after the calculated end-point had been reached. As to the amount of chromium nitrate which was added the following may be said: the maximum amount of foreign metal which was safely present in the iron solution without causing difficulty in the location of the end-point depended on the amount of chromium added. It was ascertained that the chromium must be present in a molar ratio of at least *one* chromium to *one* metal. Small quantities of iron, even in the absence of foreign metals, gave a heterometric curve with a slightly rising maximum density line. In this case, too, the addition of chromium was helpful, the maximum density line being strictly horizontal. On the other hand, the addition of large excesses of chromium decreases the maximum density value and impedes the determination.

As to the additional critical point obtained at the molar ratio of *one* iron to *one* aluminon (see previous report), this point almost disappeared in the presence of

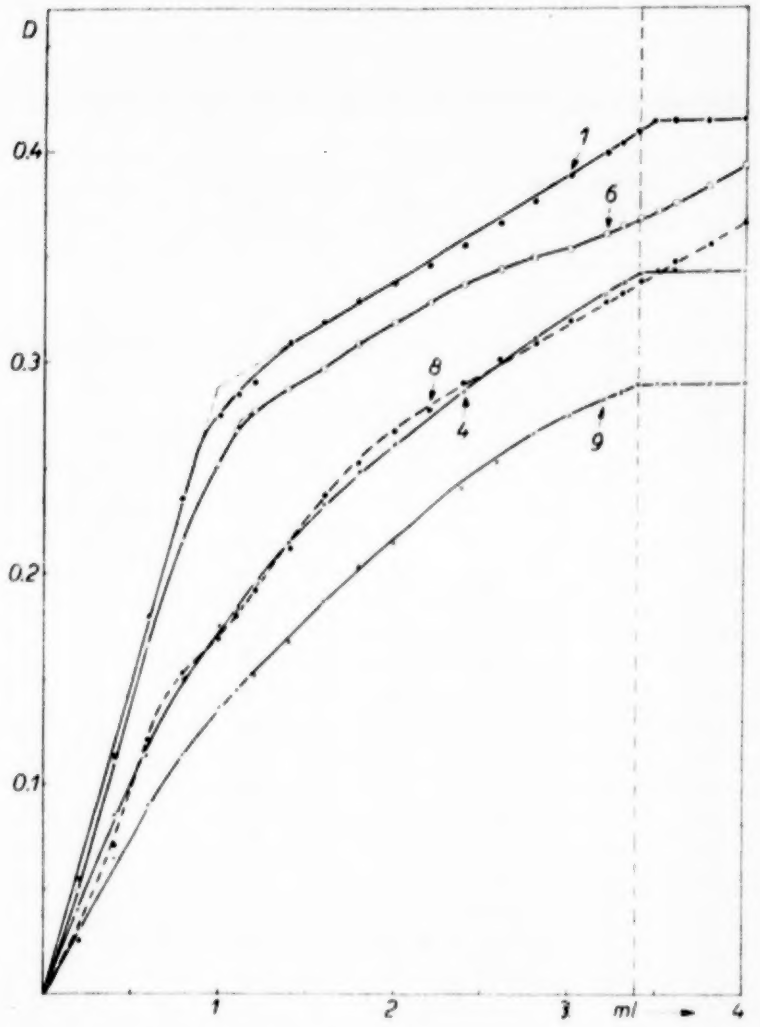


Fig. 1. Titrations of iron with aluminon in excesses of chromium and aluminium.

chromium. In specific cases it could be located from the curves by extrapolation, but the location was very uncertain.

Titrations in the presence of trivalent cations

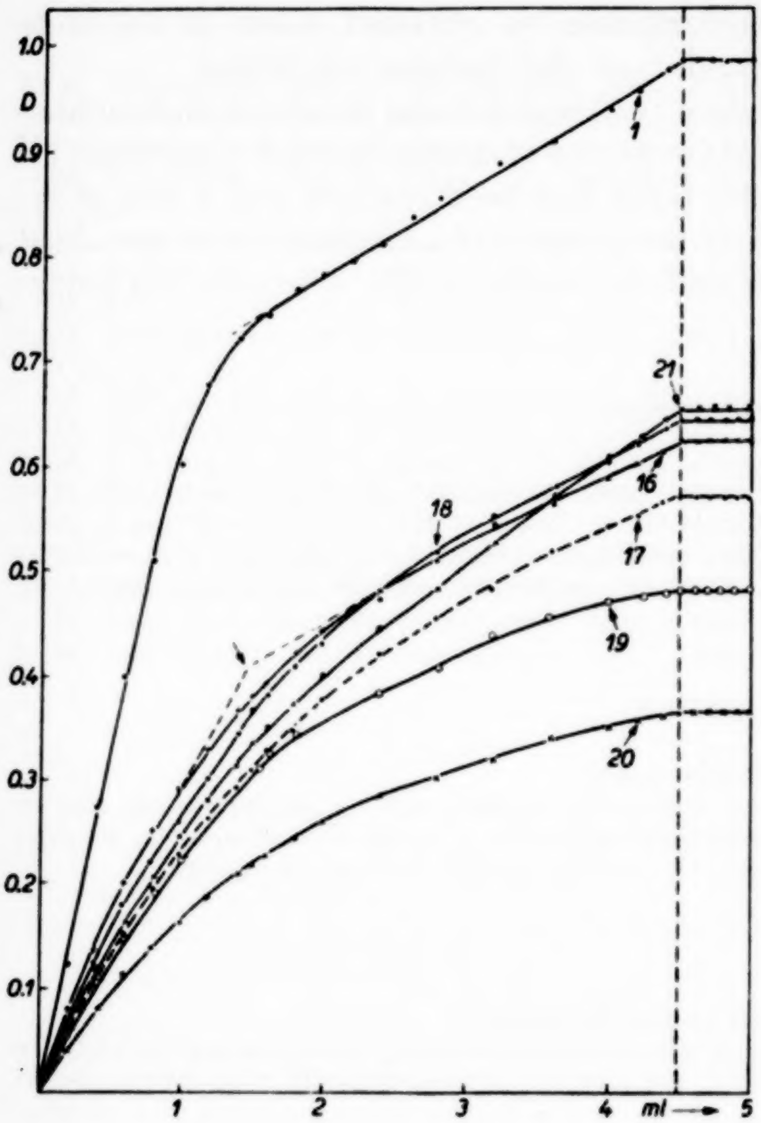
Table 1 and Figs. 1 and 2 give results with aluminium and chromium.

In the presence of aluminium alone (without chromium) the curves showed no end-point for iron, even when the latter was present in large amounts (Table 1, expts. 6-8 and Fig. 1). The addition of chromium nitrate makes the determination easy and safe. The solution could contain 99.5% aluminium, the error was 0.6% or zero (expts. 9 and 7). The maximum density values obtained decreased somewhat in comparison with the blanks (expts. 1 and 15), therefore the use of a higher amount of iron for the analysis is preferable (expt. 17).

In the presence of chromium. The content of chromium could be 99.5%. The titration time was 10 minutes and the error was zero (expt. 16). The maximum density value is reduced by one third.

Titrations in the presence of bivalent cations

The iron could by analysed in the presence of 99.5% of the following foreign metals: Pb, Cd, Cu, Co, Ni, Mn, Zn, Mg, Ba, Ca. To all solutions analysed, an amount of chromium nitrate must be added, which is equal or exceeds mole to mole the amount of the sum of the foreign bivalent cations. An excess of chromium caused no harm to the precision of the determination; 0.2-0.5 mg iron had to be used for the analysis.



With the higher amounts of iron the determination could be carried out with an error equal to zero.

On the specific action of chromium

It can be seen from the material presented that iron can be analysed in the presence of foreign metals *only after the addition* of *chromium nitrate*. The question arises, what is the specific action of chromium and how can that action be interpreted?

From previous work on aluminon it is known that chromium forms insoluble complex compounds with aluminon which are probably next in stability to the compounds similar to iron. The chromium complexes are therefore probably formed (in the presence of excesses of foreign metals) with the excess of aluminon *after* the quantitative precipitation of $Fe(AN)_3$ has occurred. There is a large excess of chromium in solution and the compound which is formed under all conditions must therefore have the composition of $Cr_1(AN)_1$. This last, however, remains *dissolved* under the working conditions described here. The excess of aluminon is therefore used up in forming the soluble chromium compound and a *horizontal* maximum density line is obtained.

Fig. 2. Titration of iron with aluminon in excesses of trivalent and bivalent salts.

Similar effects were obtained with trivalent phthalates[4]. At the *same*

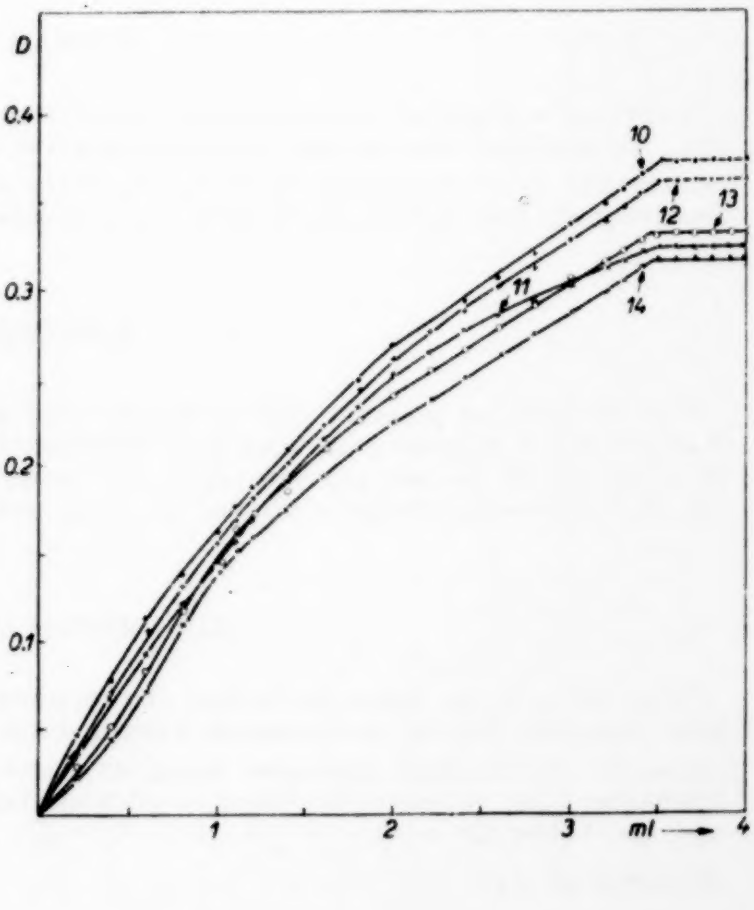


Fig. 3. Titrations of iron with aluminon in excesses of bivalent salts.

References p. 445.

composition and concentration of the complexes we obtained either an insoluble or a soluble compound, and this depended on the working conditions.

On the other hand, when a dilute solution of an iron salt was titrated with aluminon even in the absence of foreign metals, the excess of aluminon itself somewhat increased the density after the maximum point had been reached and a line of increasing density may be obtained. Due to the presence of a chromium salt the added aluminon is bound to the chromium and we obtain a safe *horizontal* maximum density line.

PROCEDURE

The solution of ferric iron which has to be analysed must be acidified with nitric acid. The molarity of nitric acid must be equal or double the molarity of the iron. The solution is then diluted to give an iron concentration equal to 0.0004M-0.001M (or 0.2-0.5 mg Fe). The analysed solution may contain, in addition to iron, other tri- or bivalent metals which may make up $\leqq$ 99.5% of the total metal content.

METHOD

1. *Analysis in the absence of excesses of foreign metals*

Ten ml of an aqueous solution of an iron salt, which contain 0.2-0.5 mg ferric iron and in addition 1 ml M acetic acid are titrated heterometrically with a 0.003-0.006M aqueous solution of aluminon. It is advisable to add 1 ml 0.1M $Cr(NO_3)_3$ to the analysed solution.

Titration time: 10-15 minutes.

Error: zero to 2%.

2. *Analysis in the presence of large excesses of foreign metals*

Ten ml of an aqueous solution of iron salt which contain 0.2-0.5 mg ferric iron and in addition 1 ml M acetic acid and 1 to 2 ml M $Cr(NO_3)_3$ are titrated heterometrically with 0.003-0.006M solution of aluminon.

Titration time: 10-15 minutes.

Error: zero to 2%

SUMMARY

A method is presented for the heterometric determination of 0.2-0.5 mg ferric iron with aluminon. The analysed solution may contain excesses of coloured or colourless foreign bi-or trivalent cations. The latter may make up $\leqq$ 99.5% of the total metal content. The working conditions were studied. The determination lasts 10-15 minutes and the error is 0-2%.

RÉSUMÉ

Une méthode est proposée pour le dosage hétérométrique du fer(III) (0.2-0.5 mg) au moyen d'aluminon. La solution à analyser peut renfermer un excès de cations bi- ou trivalents colorés ou incolores; ces derniers peuvent représenter jusqu'à 99.5% du total. Les conditions de travail ont été étudiées. Le dosage s'effectue en 10-15 minutes. L'erreur est de 0 à 2%.

ZUSAMMENFASSUNG

Eine Methode zur heterometrischen Bestimmung von 0.2-0.5 mg Eisen(III) mit Aluminon wird vorgelegt. Die zu analysierende Lösung kann Überschüsse von gefärbten oder farblosen zwei- oder dreiwertigen Kationen enthalten. Letztere können $\leqq$ 99.5% vom Gesamtgehalt ausmachen. Die Arbeitsbedingungen wurden studiert. Die Bestimmung dauert 10-15 Minuten und der Fehler ist 0-2%.

References p. 445.

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COLORIMETRIC DETERMINATION OF OSMIUM(VI) WITH 1-NAPHTHYLAMINE-3,5,7-TRISULFONIC ACID

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INTRODUCTION

The importance of osmium in the fields of metallurgy[3,4,6], biology[3], medicinal chemistry[1], and possibly chemotherapy[7] justify search for a colorimetric method which is both simple and precise for its quantitative determination. Although a number of reactions have been proposed for the determination of osmium, the ones that have been developed leave much to be desired. Of the colorimetric reagents now available, thiourea is by far the best suited for analytical application and has been the one most commonly used.

We have developed a new colorimetric method based on the stable violet complex formed by the reaction of osmium (OsO_4^{-2}) with 1-naphthylamine-3,5,7-trisulfonic acid. Further work must be carried out to determine whether or not the method herein proposed is of general use, because it requires that the osmium be in the VI valence state and this limits the application of the reagent. Our investigation shows, however, that the reagent is useful for the identification of hexavalent osmium and for its quantitative determination in trace quantities. Compared with colorimetric methods described in the literature the new method has a higher sensitivity (1 part of osmium in 15,000,000 parts of solution). Other advantages are simplicity of operation and the fact that the reaction is carried out in weakly acidic medium (adjusted to pH 1.5) in contrast to a strongly acid one required for the thiourea method, for example. The chief disadvantage is the limitation of the color reaction to VI valent osmium.

APPARATUS

All absorbance measurements were made with a Beckman spectrophotometer, Model DU, using matched 1.00 cm Corex cells. At wavelengths of 625 mμ or below, the ultraviolet-sensitive phototube was used; above 625 mμ, the red-sensitive phototube. The phototube circuit was kept at maximum sensitivity and under these conditions the slit width at 560 mμ was about 0.04 mμ, corresponding to a nominal band width of 2.3 mμ.

A Beckman pH meter, Model G, was used for all pH measurements. The meter was calibrated from time to time, using Leeds and Northrup standard buffer of pH 4.

REAGENTS

Standard osmium solution. A standard solution containing 100 p.p.m. osmium was prepared by dissolving 0.0196 g of potassium osmate ($K_2OsO_4.2H_2O$), obtained from American Platinum Works, in distilled water and diluting to the mark in a 100 ml volumetric flask. According to FRIEND[2], this solution is quite stable, though we observed some evidence of decomposition, a small black deposit appearing at the top of the volumetric flask after about one week. At higher temperatures, about 31° C, the solution is much less stable, the osmate decomposing into the volatile osmium tetroxide and osmium dioxide or metallic osmium. For best results the solution should be kept between 15° and 25° C. Over this temperature range no decomposition was noted.

Reagent solution. $5.3 \cdot 10^{-4} M$. Dissolve 0.0505 g of 1-naphthylamine-3,5,7-trisulfonic acid in water, dilute to 250 ml and mix. The compound may be obtained from the LaMotte Chemical Products Co., Towson, Baltimore, Md. (U.S.A.).

Buffer solutions. Buffer solutions were the Clark and Lubs type, prepared by mixing 97 ml of $0.2N$ hydrochloric acid and 50 ml of $0.2N$ potassium chloride and diluting to 200 ml.

Other reagents. All other reagents were of analytical grade and were used without further purification.

EXPERIMENTAL

Absorbance curves. An absorbance curve of the reagent solution ($5.3 \cdot 10^{-4} M$) is shown in Fig. 1. The reagent absorbs only in the low wavelength portion of the visible region and at the maximum for the organo-osmium complex its absorbance is negligible. Hence excess reagent does not appreciably increase the absorbance reading of the solution. Experiments showed that the amount of excess is not important provided a 7 : 1 ratio is not exceeded.

Fig. 1 also shows an absorbance curve for the organo-osmium complex. The complex was formed by adding excess reagent to 4 p.p.m. osmium as OsO_4^{-2}. The curve shows a sharp peak at 560 mμ.

Effect of pH. The organo-osmium complex shows wide variation with change in pH, having maximum absorbance at pH 1.5. The purple color first formed upon addition of the reagent to a solution of osmium(VI) changes to violet at pH 1, to blue at higher pH values and finally to a pale green at pH 10 to 11.

Rate of reaction and stability of the complex. The formation of the organo-osmium complex was found to be dependent upon the reaction time. The color intensity increased up to four hours, after which the absorbance remained nearly constant. Absorbance readings of the colored complex taken over a period of one month showed no significant change; a stability quite adequate for analytical applications.

Beer's law. The organo-osmium complex adheres to Beer's law over an osmium concentration of 0 to 6 p.p.m., with a practical range of 1.5 to 5.5 p.p.m., corresponding to absorbance readings of 0.2 to 0.7 unit.

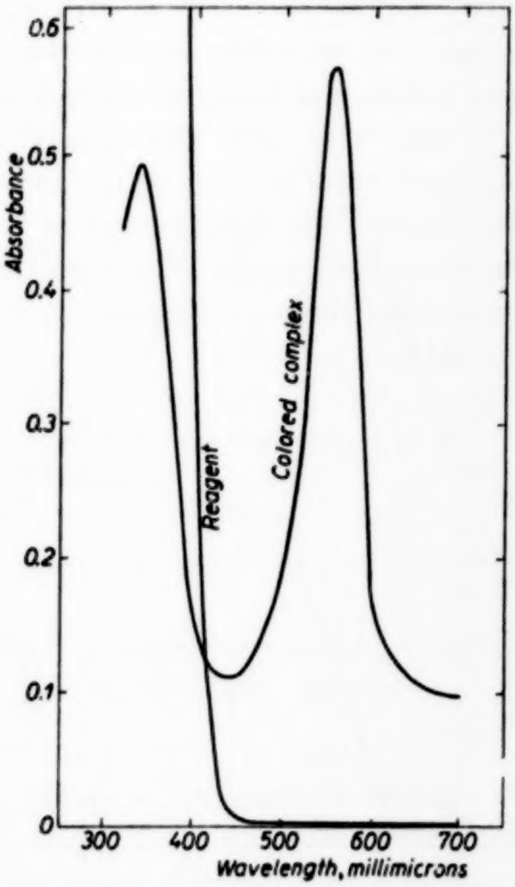

Fig. 1. Absorbance curves for 1-naphthylamine-3,5,7-trisulfonic acid and for its osmium(VI) complex, respectively.

Sensitivity. According to SANDELL's expression of sensitivity[9] and using an absorbance value of 0.119 for 1 p.p.m. osmium, the sensitivity is 0.01 γ per sq cm. However, for general use, the practical sensitivity is 0.067 γ per sq cm, *i.e.*, 1 part of osmium in 15,000,000 parts of solution. Six solutions containing this concentration of osmium gave absorbance readings of 0.009, 0.010, 0.012, 0.011, 0.005, and 0.010 unit, respectively.

Effect of temperature and order of adding solutions. Allowing maximum color intensity of the complex to develop over a temperature range of 15° to 35° C, the absorbance of the complex developed at 35° C was a little higher than at 15° C, but not enough to warrant raising the temperature above room temperature for color development.

Time for maximum color development of the complex must be allowed before the buffer is added to adjust the pH to 1.5; failure to do so results in decrease in absorbance.

Diverse ions. To determine interference by diverse ions, solutions were prepared containing 4 p.p.m. osmium, reagent, and varying concentrations of each ion to be tested. An increase or decrease of 0.005 unit in absorbance was taken as an interference. The following ions in concentration greater than 1 : 1, were found to cause an interference: Ru^{+3}, Rh^{+3}, Pd^{+2}, Ir^{+4}, Pt^{+4}, Al^{+3}, VO^{+}, Cr^{+3}, Fe^{+3}, Fe^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Pb^{+2}, Mn^{+2}, Mg^{+2}, and Ag^{+}. These results indicate that osmium must be separated from many of the metallic ions before it can be determined by this method.

Results of analysis. Ten solutions containing 4 p.p.m. osmium as OsO_4^{-2} were treated according to the proposed procedure and their absorbance measured at 560 mμ. The average absorbance was 0.564 unit, with an average deviation of 0.001, *i.e.* a relative deviation of about 0.2%, a precision which is quite good.

Osmium complex in solution. Three methods were employed to establish the empirical formula of the complex *in solution*. These were the mole ratio method of Yoe and Jones[13], the continuous variations method of Job[8] with modification by Vosburgh and Cooper[12] and the slope ratio method proposed by Harvey and Manning[5]. Results of the three methods indicate a complex formed by two molecules of reagent reacting with one osmate ion. The several irregular points on the curves are probably due to the fact that when excess osmium(VI) is present in acid solution it tends to reduce to colloidal oxides or metallic osmium.

In the Yoe and Jones method a series of solutions is prepared containing a constant amount of metallic ion but with increasing ratios of reagent to metal (or *vice versa*). The absorbances of the solutions are measured and plotted against the concentration ratios. The resulting curve should be a straight line rising until the combining ratio of reagent to metal ion is reached, after which it should break abruptly.

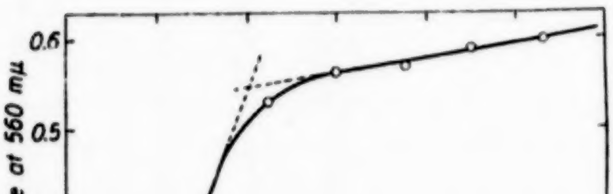

Fig. 2. Ratio of reagent to osmium by the "mole ratio" method.

Applying this method to the organo-osmium complex, solutions were made in which the osmium concentration was kept constant at $5.3 \cdot 10^{-4} M$ and the ratio of moles of reagent to moles of osmium varied from 0.7 to 5.2. A water blank was used for all absorbance measurements at 560 mμ. In Fig. 2 the results show a 2 to 1 ratio of reagent to osmium.

Job's method of continuous variations involves the preparation of a series of solutions in which the mole per cent of two substances forming a compound is varied and a physical property of the solution is measured. The physical property measured in this investigation is the absorbance of light at a given wavelength. A plot of the difference between the observed value and the value calculated assuming no reaction, should show a maximum or a minimum at the mole percent corresponding to the compound formed.

In applying this method to the organo-osmium complex, solutions were prepared containing X ml, of a $5.3 \cdot 10^{-4} M$ reagent solution and $6\text{-}X$ ml of a $5.3 \cdot 10^{-4} M$ osmium solution. After standing four hours, buffer was added, the solution diluted to 25 ml with distilled water and mixed. Absorbances of the solutions were then measured at 560 mμ. If the formation of the osmium complex is represented as follows, where n may be any number and R indicates reagent,

$$\text{Os} + nR = \text{Os}R_n$$

and the function Y is such that

$$Y = \text{A}_\text{s}(\text{obs.}) - \text{A}_\text{s}(\text{calc.}),$$

then a plot of the function Y against X should show a maximum (or minimum) at a point where

$$\frac{X}{6\text{-}X} = n.$$

Results as shown in Fig. 3, indicate a reagent to osmium ratio of 2 to 1. Here $X = 4$, hence $n = 2$.

The slope ratio method of HARVEY AND MANNING employs two sets of solutions. In the first set, the concentration of one of the reactants is maintained constant and in excess, while the concentration of the other is varied. In making the second set, the same procedure is followed but the moles of the two reactants are reversed. The absorbance of each solution is measured and plotted against concentration of the variable reactant.

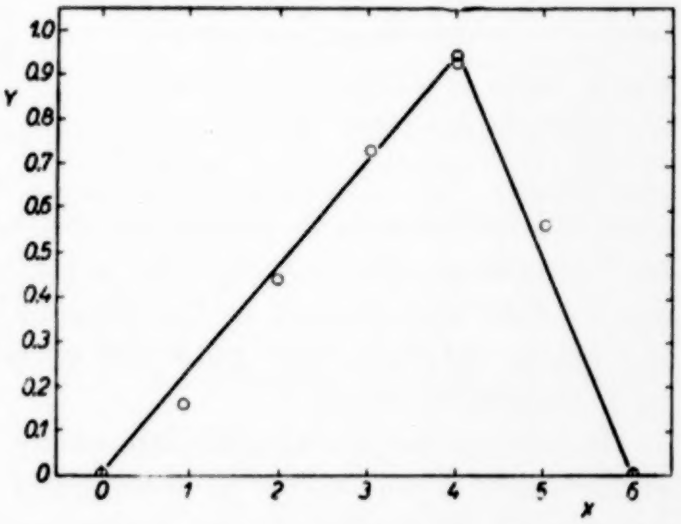

Fig. 3. Ratio of reagent to osmium by the "continuous variations" method.

The slope ratio method was applied to the organo-osmium complex as follows: One series of solutions was prepared containing 20 p.p.m. of osmium (an excess), buffer, and varying concentrations of reagent. Absorbance readings of the solutions were measured against a water blank at 560 mμ. Another series of solutions were prepared in which the reagent concentration was constant and in excess, buffer was added and the amounts of osmium varied. Absorbances were measured against a reagent blank. Results are shown in Fig. 4. The ratio of the two slopes should be equal to the ratio of reagent to metal:

$$\frac{\text{Slope 2}}{\text{Slope 1}} = \frac{\text{reagent}}{\text{osmium}}$$

From the data of Fig. 4, slope 2 = 0.1082 (reagent in excess) and slope 1 = 0.0560 (osmium in excess) and the reagent to osmium ratio is therefore

$$\frac{0.1082}{0.0560} = 1.93 \text{ — } \textit{i.e.}, \text{ a ratio of 2 to 1 (within the limits of error).}$$

The results of the three methods indicate that *in solution* the ratio of reagent to osmium is 2 to 1. Solutions of 1-naphthylamine-6-sulfonic acid and 1-naphthylamine each give the characteristic purple color with osmium(VI), the latter precipitating after standing about a half hour. This indicates that the colored compound produced by osmium(VI) and 1-naphthylamine-3,5,7-trisulfonic acid is the result of a reaction at the amino group.

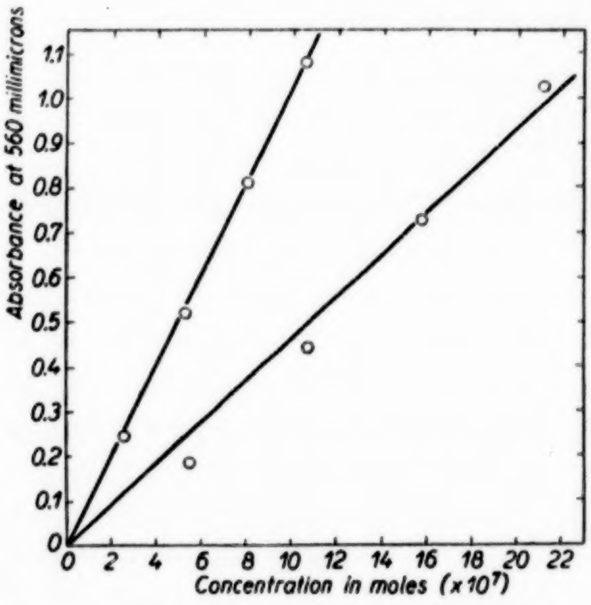

Fig. 4. Ratio of reagent to osmium by the "slope ratio" method.

Attempts at quantitative separation and determination of osmium in the hexavalent state. Two methods have been employed for the quantitative separation of osmium from all other elements. These are distillation[3,11] and extraction with chloroform[10]. Both methods separate osmium in the octavalent state. Since the determination with 1-naphthylamine-3,5,7-trisulfonic acid requires that the osmium be present in its hexavalent state, the problem is to reduce the osmium quantitatively from the octavalent to the hexavalent state. Attempts to do this met with no success. Whenever reducing agents were first applied to the osmium(VIII) solutions and then reagent added, the colors obtained were light red or orange instead of violet. In some cases no color developed at all.

The general use of 1-naphthylamine-3,5,7-trisulfonic acid as a reagent for osmium is dependent upon success in obtaining a quantitative reduction of osmium to the hexavalent state after its separation from other elements. If a suitable reducing agent can be found, it should be possible to apply the proposed colorimetric method to determine osmium in any material after its isolation either by distillation or extraction. Work along these lines is being continued.

SUMMARY

An investigation has been made of the organic compound, 1-naphthylamine-3,5,7-trisulfonic acid, for use as a colorimetric reagent for the determination of trace quantities of osmium(VI). When this compound is added to an osmium (OsO_4^{-2}) solution, a violet colored organo-osmium complex is formed which has highest sensitivity at wavelength 560 mμ. The complex reaches maximum color intensity after four hours. The solution should be brought to pH 1.5 and maintained at this pH with a buffer, after maximum color development. The colored complex conforms to Beer's law over an osmium concentration range of 0 to 6 p.p.m. Its absorbance is not affected by either excess reagent (up to a 7 : 1 ratio) or by temperature variation over the range 15° to 35° C. Many metallic ions interfere with the color reaction and hence require a separation of osmium from these ions.

The nature of the complex *in solution* was studied by the following three methods: (1) mole ratio, (2) continuous variations and (3) slope ratio. All three methods indicate a ratio of reagent to osmium of 2 to 1.

A procedure for the colorimetric determination of osmium(VI) has been developed; it has a sensitivity of 1 part osmium in 15,000,000 parts of solution, with good precision.

RÉSUMÉ

Une étude a été effectuée sur l'acide 1-naphtylamine-3,5,7-trisulfonique, comme réactif colorimétrique pour le dosage de traces d'osmium(VI). Ce réactif donne avec l'osmium (OsO_4^{-2}) un complexe de coloration violette qui présente le maximum de sensibilité à la longueur d'onde de 560 mμ. La coloration du complexe formé atteint son maximum d'intensité après quatre heures. La solution doit être portée au pH 1.5 et maintenue à ce pH à l'aide d'un tampon, après le développement maximum de la coloration. La coloration obtenue suit la loi de Beer pour des concentrations d'osmium allant de 0 à 6 p.p.m. L'absorption n'est pas gênée par un excès de réactif (jusqu'à un rapport 7:1) ou par une variation de température de 15 à 35° C. Plusieurs ions métalliques gênent, ce qui nécessite une séparation de l'osmium. La nature du complexe *en solution* a été étudiée par trois méthodes différentes. Toutes ces méthodes indiquent un rapport réactif/osmium de 2/1. Un procédé de dosage colorimétrique de l'osmium(VI) est proposé; on arrive à une sensibilité de 1 partie d'osmium pour 15,000,000 parties de solution, avec une bonne précision.

ZUSAMMENFASSUNG

Es wurde eine Untersuchung ausgeführt über die 1-Naphtylamin-3,5,7-trisulfonsäure, als kolorimetrisches Reagenz für die Bestimmung von Spuren von Osmium(VI). Dieses Reagenz gibt mit dem Osmium (OsO_4^{-2}) einen violetten Komplex, welcher die grösste Empfindlichkeit bei der Wellenlänge 560 mμ aufweist. Die Färbung dieses Komplexes erreicht ihre maximale Intensität nach vier Stunden. Die Lösung muss auf pH 1.5 gebracht und mit Hilfe einer Pufferlösung auf diesem pH gehalten werden nachdem die stärkste Farbintensität erreicht ist. Die Färbung folgt dem Beerschen Gesetz für Konzentrationen von Osmium von 0-6 p.p.m. Die Absorption wird durch einen Überschuss an Reagenz (bis zu einem Verhältnis von 7:1) oder durch Temperaturschwankungen zwischen 15-35° nicht gestört. Mehrere Metallionen stören, was die Abtrennung des Osmiums verlangt. Die Art des Komplexes *in Lösung* wurde mit Hilfe von drei verschiedenen Methoden untersucht. Alle diese Methoden geben ein Verhältnis Reagenz/Osmium, 2/1. Es wird ein Verfahren zur kolorimetrischen Bestimmung von Osmium(VI) vorgeschlagen. Man erreicht eine Empfindlichkeit von 1 Teil Osmium in 15,000,000 Teilen Lösung, mit einer guten Präzision.

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THE DETERMINATION OF MICROGRAM QUANTITIES OF FLUORIDE
V. THE USE OF THE ALUMINIUM-CHROMEAZUROL-S COMPLEX

by

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In the previous paper[1] in the present series the aluminium chromeazurol S complex was suggested as a sensitive reagent for the determination of fluoride; it was not however expected to be as sensitive as the aluminium-eriochromecyanin complex, and the latter reagent was tested first. As difficulties were encountered during the development of the method using the aluminium-eriochromecyanin complex it was decided to try out the present method and the development of the two methods was completed simultaneously. In practice the chromeazurol S method has proved more sensitive than expected and in some ways has advantages over the one using eriochromecyanin although for ultimate sensitivity the latter is preferred.

EXPERIMENTAL

The previous work on haematoxylin[2,3] and eriochromecyanin[1] had indicated that when using an aluminium-dye system as reagent for the determination of fluoride the best results were obtained at pH values of 4.0-4.7 and preliminary experiments showed that with the present system the most satisfactory complex was obtained at a pH of 4.25. The complex tends to precipitate on standing but addition of gum arabic produces a satisfactory stock solution of complex which is stable over a period of several weeks. The complex has a comparatively sharp peak at 5500 Å.

The effect of a change in ionic strength of solutions used was found to be similar to that experienced in the case of the eriochromecyanin complex and was again overcome by increasing the ionic strength of the solutions sufficiently to swamp minor variations; this was done as before by making the stock $0.5M$ and the buffer $2M$ with respect to ammonium chloride.

REVINSON AND HARLEY[4] used the thorium salt of chromeazurol S in a similar manner to determine fluoride. We have tried their method and in general confirm their findings. The thorium complex behaves much as expected.

METHOD

A. *Reagents*

(i) *Standard fluoride solution*

Dissolve 0.5525 g of sodium fluoride in water and dilute to 250 ml. Dilute 1 ml of this solution to 100 ml.

1 ml = 10 μg F.

The purest available material should be used; that supplied by BAKER AND ADAMSON to A.C.S. specification is suitable.

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* Present Address: The Director, M.O.S., Tropical Testing Establishment, Port Harcourt, Nigeria.

References p. 456.

(ii) *Standard aluminium solution*
Dissolve 1.867 g "AnalaR" quality aluminium ammonium sulphate ($AlNH_4(SO_4)_2.12H_2O$) in water and dilute to 100 ml.
1 ml = 1.11 mg Al.
For use dilute 10 ml of the above solution to 100 ml.
1 ml = 111 μg Al.

(iii) *Chromeazurol S solution* 0.275%
Dissolve 0.275 g of solid in 10 ml of 0.1*M* hydrochloric acid and dilute to 100 ml.

(iv) Ammonium hydroxide 9*M*

(v) Glacial acetic acid

(vi) *Gum arabic* 5%
Dissolve 5 g of finely crushed solid in approximately 80 ml of freshly boiled water at 70° C *(ca.)*. Filter while still hot through glass wool and dilute to 100 ml with freshly boiled water.

(vii) *Buffer solution* (pH 4.25)
Dissolve 32 g "AnalaR" quality ammonium chloride in 200 ml of water. Add 40 ml glacial acetic acid and 10 ml concentrated ammonia (sp.gr. 0.88). Cool to room temperature and adjust pH to 4.25 by further addition of ammonia using a pH meter. Dilute to 300 ml, check pH and again adjust to 4.25 if necessary.

B. *Procedure*

(a) *Preliminary treatment*
Separate the fluoride from interfering ions, if necessary, by distillation from sulphuric acid in the presence of silica according to the method of WILLARD AND WINTER[5]. Collect 160 ml of distillate. If a micro-apparatus such as that described by HORTON THOMASON AND MILLER[6] or by MACNULTY AND BARRETT[7] is used only 10-20 ml need collected. Treat distillate as described below.

(b) *Treatment of distillates*

(I) *For distillates of acid content equivalent to less than 1 ml of 1M acid per 150 ml*
This applies also to samples where distillation is not necessary, *e.g.* water.
- (i) Neutralize the distillate to phenolphthalein with 0.1*M* sodium hydroxide. Record the volume of the neutralized solution and the volume of alkali used.
- (ii) Prepare a blank solution by neutralizing a volume of 0.1*M* sodium hydroxide equal to that used in step (1) with 0.05*M* sulphuric acid using phenolphthalein as indicator. Dilute the solution to a volume equal to that of the neutralized distillate.

(II) *For distillates of high acid content*
- (i) Add sufficient 9*M* ammonium hydroxide to the distillate to bring the pH to 7 and note the volume required. Add 1 ml of glacial acetic acid and adjust the pH to 4.25 by further addition of ammonium hydroxide and again note the volume used.
- (ii) Prepare a blank solution by adding 1 ml of glacial acetic acid to a volume of 9*M* ammonium hydroxide equal to the total amount used in step (1). Add acid (of the kind present in the distillate) to bring the pH to 4.25. Dilute the solution to a volume equal to that of the neutralized distillate.

(c) *Determination of fluoride*
- (i) Place a suitable volume of the neutralized distillate in a 50 ml flask and an equal volume of blank solution in a second 50 ml flask. Add 2 ml of buffer solution to each flask and mix well.
- (ii) Into each flask pipette 15 ml aluminium-chromeazurol stock solution (see paragraph C.). Make up to the mark with water and mix well.
- (iii) Place flasks in a water bath at 60° for 15 minutes. Cool to room temperature by immersion in a cold water bath.
- (iv) Measure the difference between the absorbancies of the two solutions using a Hilger-Spekker absorptiometer with yellow green 605 filters and 2 cm cells, or a similar suitable instrument.
- (v) Calculate the fluoride present by reference to a prepared calibration graph.

C. *Preparation of aluminium-chromeazurol stock solution*

To 425 ml of water in a 600 ml beaker add in order the following mixing well after each addition.

(i) 13.4 g ammonium chloride
(ii) 3 ml glacial acetic acid
(iii) 25 ml gum arabic solution (5%)
(iv) 20 ml 0.275% chromeazurol S solution
(v) 10 ml standard aluminium solution (111 μg Al/ml)

Slowly and carefully, with adequate stirring, add 1.8M ammonium hydroxide to bring the pH to 4.25 using a pH meter. Make up to 500 ml and filter through a No. 40 fluted filter paper. Add a few crystals of thymol to prevent mould growth.

D. *Calibration*

(i) Into each of six stoppered measuring flasks (numbered 1-6) of 50 ml capacity pipette 2 ml of buffer solution (pH 4.25).
(ii) Add standard fluoride solution to the flasks to give fluoride content as follows:

Flask No.	1	2	3	4	5	6
μg F	0	4	8	12	16	20

(iii) Add to each 30 ml of water.
(iv) Add 15 ml of aluminium-chromeazurol S stock solution to each flask, make up to the mark with water and mix well.
(v) Heat on a water bath at 60° C for 15 minutes. Then cool to room temperature by placing in a bath of cold water.
(vi) Measure the difference between the absorbancy of each fluoride containing solution and that containing none using a Hilger-Spekker absorptiometer with yellow green 605 filters and 2 cm cells, or a similar suitable instrument.
(vii) Plot a calibration curve of the difference in absorbancy against fluoride concentration. Two typical calibrations are recorded in Table I.

INTERFERENCES

The system used in this method is basically the same as the aluminium-eriochromecyanin and aluminium-haematoxylin methods and it is therefore to be expected that the ions interfering with the present method would be the same, as was found with these methods.

RESULTS AND DISCUSSION

Two typical calibration curves for the method are shown in Table I, and Table II shows a series of recoveries under normal conditions of use. These figures give a good idea of the accuracy and reproducibility of the method. The overall standard deviation for the range 0-18 μg fluoride is 0.46 μg (this figure is taken from a forthcoming paper on a statistical comparison of fluoride methods). Thus 0.9 μg should just be detectable with certainty in 50 ml of final solution, and this amount of fluoride must be present in the amount of treated distillate taken for the determination. In the case of macrodistillation the volume of distillate after neutralization is of the order of 170 ml and about 30 ml of this can be used for fluoride determination. The sample must therefore contain a minimum of 5.4 μg of fluoride. In a macrodistillation there is no difficulty in handing 25 g of sample and this gives a limit of detection of fluoride of about 0.2 p.p.m.; the method is thus only about half as sensitive as the eriochromecyanin one. Using a microdistillation where the whole of the distillate can be used for the determination, and modifying the technique to keep dilution a minimum, the limit of detection can be lowered to 0.1 p.p.m. or less.

A similar method which uses the thorium chromeazurol complex has recently been published by Revinson and Harley[4]. The change in absorbancy obtained for 10 μg fluoride by these authors using the thorium salt appears to be only half that

References p. 456.

TABLE I

TYPICAL CALIBRATIONS FOR THE ALUMINIUM CHROMEAZUROL METHOD

μg F		0	4	8	12	16	20
Absorbancy x 10^3	a	0	124	227	327	437	540
	b	0	125	234	328	444	538

TABLE II

TYPICAL RECOVERIES OF FLUORIDE (μg) BY THE ALUMINIUM CHROMEAZUROL METHOD

F added	*F recovered*	*F added*	*F recovered*
3.0	3.2	11.0	11.4
	3.2		10.9
	3.2		10.9
	3.0		10.9
	2.8		
	2.8	18.0	17.3
	3.0		17.6
	3.2		17.8
	2.9		18.1
	2.9		17.3
	2.3		18.0
			18.1
11.0	10.9		18.6
	11.4		17.5
	10.9		18.4
	11.3		18.0
	10.3		18.0
	10.4		17.2
	11.2		17.9
	11.9		17.8

obtained when the aluminium salt is used and the standard deviation of the former method seems to be somewhat larger than that using aluminium although no actual figure is quoted. The standing for two hours makes the thorium method considerably longer than the aluminium one but it is probable that the standing time of two hours quoted by REVINSON AND HARLEY could be considerably curtailed by employing a short period of heating as has been done by ourselves.

The mechanism of reactions involved in this method is expected to be similar to those put forward in our previous papers. A chelate compound is first formed between the dye ion and the aluminium which is subsequently destroyed by fluoride. Under the conditions of the method the aluminium and fluoride appear to be combined in the ratio 1:2 and the chelate compound appears to have the formula Al $(\text{dye})_2$.

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The Authors wish to thank Mr. A. S. NICHOLSON for his interest and encouragement.

SUMMARY

A spectrophotometric method for determining fluoride using the aluminium chromeazurol complex is described. Fluoride in solution free from interfering ions or obtained by distillation as hydrofluosilicic acid is determined by destruction of the complex, the amount destroyed being directly proportional to the fluoride present. The method will detect as little as 0.02 μg/ml of fluoride and with 0-20 μg in the final solution fluoride can be determined with an accuracy of $\pm$ 0.6 μg.

References p. 456.

RÉSUMÉ

Une méthode spectrophotométrique est décrite pour le dosage de l'anion fluorhydrique au moyen du complexe aluminium-chromazurol-S. L'anion fluorhydrique, en l'absence d'ions gênants, ou séparé par distillation sous forme d'acide fluosilicique, est déterminé par décomposition du complexe, la quantité décomposée étant directement proportionnelle à la quantité de fluorure présent. Cette méthode permet de déceler jusqu'à 0.02 μg/ml de fluorure. Des quantités de F^- allant de 0 à 20 μg peuvent être dosées avec une précision de ± 0.6 μg.

ZUSAMMENFASSUNG

Eine spektrophotometrische Methode für die Bestimmung des Fluorid-Anions mittels eines Aluminiumchromazurol-S Komplexes wird beschrieben. Das Fluorid-Anion wurde in Abwesenheit von störenden Ionen, oder abgetrennt mittels Destillation in Form von Fluorkieselsäure, durch Zersetzung des Komplexes bestimmt. Die Menge, welche zerstört wurde, war direkt proportional der Menge an Fluor. Diese Methode erlaubt Fluoridmengen bis zu 0.02 μg/ml nachzuweisen. Mengen von F^- zwischen 0-20 μg können mit einer Präzision von ± 0.6 μg bestimmt werden.

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INFLUENCE OF ORGANIC BASES ON THE PARTITION OF INDICATOR ACIDS (AND VICE-VERSA) IN A WATER-CHLOROFORM SYSTEM

ANALYTICAL APPLICATIONS

by

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In a series of previous papers[1] we discussed the ability of several indicator acids (Δ) to react with organic bases (B) yielding coloured compounds (BΔ) largely soluble in organic solvents, and we also explained how we can take advantage of the behaviour of those compounds in order to achieve the accurate titration of salts of organic bases in a water-chloroform system. The transformation interval of BΔ compounds (termed "amphindicators") *i.e.* the pH limits, between which a displacement of the colour occurs from one phase to the other, being connected to solubility problems[2], an attempt has been made to study quantitatively the influence of organic bases on the partition ratio of the indicator acids we are concerned with, in a water-chloroform system as a function of pH. Full advantage has been taken of the opportunities offered by these investigations, thanks to which it has been possible to further explore our subject by conversely studying the influence of indicator acids on the quantitative distribution of several organic bases between the above two solvents.

The first part of the present paper includes a brief description of the experimental path followed, the results obtained, and the general conclusions derived. The second part deals with a number of analytical applications based upon the above data.

From our previous qualitative investigations on the possible combinations of a dozen indicator acids with a dozen alkaloids it has been proved that generally speaking, all compounds of this type behave in an analogous fashion in the case we are dealing with. For this reason the following quantitative experiments were limited to only the compounds of bromothymol blue with the bases: procaine, strychnine, ephedrine, quinidine and atropine.

Influence of procaine base on the partition solubility of bromothymol blue (BTB) in a water-chloroform system

The partition of the dye between equal volumes of water and chloroform in various hydrogen-ion concentrations was determined first.

Reagents:

1. $5 \cdot 10^{-3}$ *molar bromothymol blue stock solution*

0.312 g of BTB (twice recrystallized from ethyl alcohol) is dissolved in a small mortar by adding 5 ml of 0.1*N* NaOH solution and further diluting with distilled water to 100 ml.

References p. 465.

2. *Comparison standard scale*

Prepared by diluting the above BTB stock-solution with 0.1*N* NaOH so as to obtain the following, decreasing by 10% dye concentrations:*

Test tube No. 1.	$2.50 \cdot 10^{-5}$ mol.	Test tube No. 9.	$1.08 \cdot 10^{-5}$ mol.
2.	$2.25 \cdot 10^{-5}$	10.	$0.97 \cdot 10^{-5}$
3.	$2.03 \cdot 10^{-5}$	11.	$0.87 \cdot 10^{-5}$
4.	$1.82 \cdot 10^{-5}$	12.	$0.78 \cdot 10^{-5}$
5.	$1.64 \cdot 10^{-5}$	13.	$0.71 \cdot 10^{-5}$
6.	$1.48 \cdot 10^{-5}$	14.	$0.64 \cdot 10^{-5}$
7.	$1.33 \cdot 10^{-5}$	15.	$0.57 \cdot 10^{-5}$
8.	$1.20 \cdot 10^{-5}$	16.	$0.51 \cdot 10^{-5}$

3. *Full series of buffer mixtures differing by 0.2 pH units*

The following solutions, the pH value of which were controlled potentiometrically, have been prepared:

From pH 1 to 3: pure hydrochloric acid solutions.
From pH 3 to 6: sodium citrate-HCl/NaOH solutions, according to SÖRENSEN.
From pH 6 to 8: KH_2PO_4-NaOH solutions, according to CLARK AND LUBS.
From pH 8 to 9: boric acid-NaOH solutions.
From pH 9.2 to 11: soda-borax mixtures, according to KOLTHOFF.
From pH 11 to 12: Na_2HPO_4-NaOH solutions, according to KOLTHOFF AND VLEESCHHOUWER.

Experimental procedure

A mixture of 4.8 ml of the chosen buffer solution, 0.2 ml. of the $5 \cdot 10^{-3} M$ BTB standard and 5 ml of chloroform was vigorously shaken in a small separator for one minute. The clear chloroform layer was transferred to a second separator and the dye retained by each solvent was determined as follows. The aqueous extract was diluted with 2*N* NaOH solution so that the colour of the liquid always fell between the limits of the standard scale, whereas the BTB dissolved in the chloroform was extracted by shaking with a suitable of 0.1*N* NaOH. By comparing the colour intensity of these two alkaline aqueous solutions with that of the standards, the BTB-molarity of each was found and the partition of the indicator between the two solvents at the chosen pH computed**. By this procedure ±2% accuracy was achieved, verified by checking the sum of the partial molarities found against the known total BTB-concentration of the system.

Curve *Δ* in Fig. 1 is a plot of the water solubility of BTB (expressed in percent) *versus* the corresponding hydrogen exponent.

We next investigated the influence of procaine base on the partition solubility of the indicator. This study was performed exactly as the preceding one, the only difference being that a suitable volume of $5 \cdot 10^{-3} M$ procaine hydrochloride solution was added to the system.

Curve *Δ*1/5 in the same graph shows the partition of BTB in the aqueous phase in the presence of a fifth of the equimolar procaine amount. Likewise, curves *Δ*1/4, *Δ*1/2, *Δ*3/4, *Δ*1, *Δ*2, *Δ*5, *Δ*10 and *Δ*50 correspond to a 0.25, 0.5, 0.75, 1, 2, 5, 10 and 50 base to acid ratio respectively.

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* The above scale, if kept in a dark place in stoppered tubes, keeps its colour intensity for several weeks. Diffused sunlight, however, gradually destroys the dye, a discolouration being observable within a short while. Unalterable artificial comparison solutions can be obtained by dissolving 0.67 g of pure $CuSO_4 \cdot 5H_2O$ in 50 ml of distilled water and diluting to a final volume of 100 ml with a 30% ammonia solution. The colour intensity of this standard corresponds to a $5 \cdot 10^{-5} M$ BTB solution (of pH 12), obeying Beer's law, within the limits of concentration we are interested in. By further diluting this stock solution with 10% ammonia, colour shades approaching those corresponding to the respective BTB molarities may be obtained.

** The colour of both layers depends on the pH of the aqueous phase. At pH's ranging over 3 the known BTB shades are observable in the H_2O-layer, varying from yellow to blue, whereas the pH must surpass the value 5.5 before any yellowish shade is perceivable in the chloroform, by which up to this pH the indicator acid is extracted in its undissociated lactonic form.

From these curves one sees that the procaine base substantially reduces the water-solubility of BTB, this effect being greater, the higher the base concentration with respect to that of indicator involved. This is in full agreement with our previous qualitative observations[2].

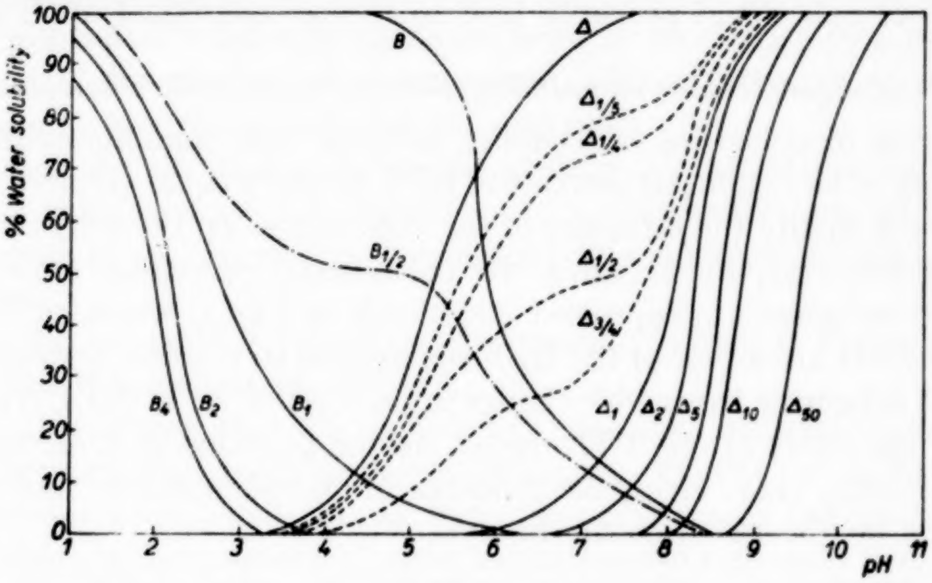

Fig. 1

What should receive the greatest emphasis when discussing this graph are the slopes characterizing the dotted curves, which correspond to the condition $[B]:[\Delta] < 1$. Indeed, the steepest points of these slopes coincide with the existing BTB excess in the aqueous phase. This leads us to the very important conclusion that under such concentration ratios, an amount of the available dye, *equimolar to the base added*, is extracted by the chloroform and, consequently, *that an indirect determination of the base could thus be possible by a colorimetric estimation of the dye dissolved in the organic phase*. By lessening the base to acid ratio, slopes become steeper, being slightly shifted towards the alkaline region, where the $CHCl_3$-solubility of BTB, when no base is present, equals zero. Hence, $[B]:[\Delta] < 0.5$ should be the most favourable condition for an accurate determination of organic bases at pH 7.2. At higher pH ranges we noticed that a fraction of the BTB amount added, always equivalent to the theoretical values, could again be extracted by the organic solvent, but a larger concentration of indicator acid was required in this case.

Thus, we had at hand a simple method, which permitted us to further explore our subject matter by conversely studying the influence of bromothymol blue on the partition of several alkaloids between water and chloroform.

Influence of bromothymol blue on the partition of procaine base in a water-chloroform system

Using the above colorimetric method, experimental details of which are given on p. 462, we firstly plotted curve B (Fig. 1), illustrating the percentual partition of pure procaine between equal volumes of water and chloroform, as a pH function. The accuracy was easily checked by the sum of the two procaine concentrations found at different pH levels which approximated by ± 2% the known base-molarity in the system.

Curves $B^1/_2$, B_1, B_2 and B_4, in the same graph, plotted from the values obtained by adding to a constant amount of base 0.5, 1, 2 and 4 mol-equivalents of indicator acid, clearly reveal the influence of BTB on the partition solubility of procaine.

The slope of curve $B^1/_2$ shows again that when Δ is less than B a quantity of base equimolar to the indicator acid added in the system is extracted by the chloroform as a $B\Delta$ compound at pH's at which, in the absence of BTB, the base is completely insoluble in this solvent. This behaviour, which is quite analogous to that observed in the opposite case could probably lead to further analytical applications.

Influence of bromothymol blue on the partition solubility of some other alkaloids and vice-versa

The partition of ephedrine, strychnine, atropine and quinidine, either alone, or in the presence of an equimolar amount of BTB, between equal volumes of water and chloroform, and finally the influence of the above bases on the solubility of the dye was investigated next, by applying the colorimetric procedure already outlined.

The results obtained are expressed graphically in Fig. 2, where curves ST*, QD, AT, PR and EPH are a plot of the H_2O-solubility of strychnine, quinidine, atropine, procaine and ephedrine bases with change in pH. Curves STΔ, QDΔ, ATΔ, PRΔ and EPHΔ show the effect of one BTB moleq. on the partition of those alkoloids, and ΔPR, ΔEPH, ΔST, ΔAT, ΔQD, the influence of an equimolar amount of the respective alkaloids on the partition of the dye.

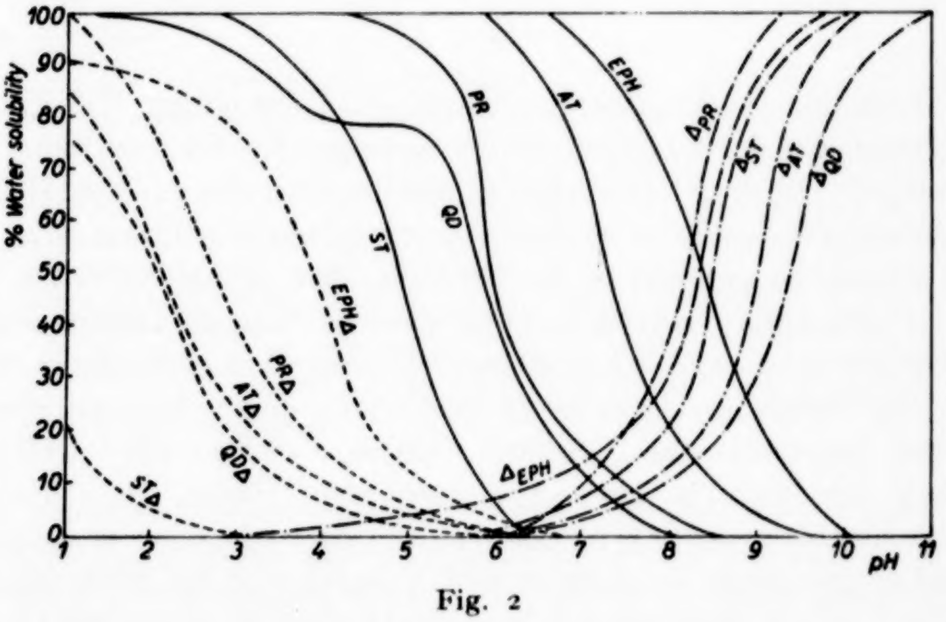

Fig. 2

This graph reveals that for every $B\Delta$ compound there exists a definite pH value only where the partition coefficients of both components are identical. Below and above this pH value each of them is partitioned according to its individual solubilities, the latter being greatly influenced by the presence of the second reactant. On the other hand, at pH areas neighbouring this value, where, as stated, $[B] = [\Delta]$ in both phases, $B\Delta$ compounds are retained in a negligible proportion in the aqueous phase. This means that a direct titration of a given organic base is possible at said narrow pH intervals, if an aqueous Δ standard solution is used as the titrant, and reciprocally.

By increasing or decreasing of the H-ion concentration $B\Delta$ compounds undergo an "acidic" or "alkaline" decomposition. The latter particularly concerns their application in "amphimetry"[1,2].

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* In carrying out our experiments with strychnine some anomalies have been encountered, due to the presence of hydrochloric acid in the buffer solution used. These anomalies, consisting of an abnormal decrease of the H_2O-solubility of strychnine were avoided by employing sulphuric instead of hydrochloric acid for buffer mixtures with pH values below 5.

APPLICATIONS

Direct titrimetric determination of alkaloids by means of indicator standard solutions

Many alkaloids and other organic bases can be directly titrated with an aqueous indicator acid standard solution. The titration must be performed in a water-chloroform system, the aqueous layer being so buffered as to restrict to a minimum the H_2O-solubility of the resulting BA compound. The appearance of a permanent colour in the aqueous phase indicates the end-point.

In some cases the titration may advantageously be carried out conversely, *i.e.* by pouring the solution under investigation into a measured volume of the indicator standard. In such cases, the end-point is noticed by a complete decolorization of the aqueous phase.

Obviously, the accuracy obtained by this method is higher, the less the water-solubility of the BA compound yielded.

Fig. 2 (p. 460) shows that the ephedrine, procaine, atropine, quinidine and strychnine tetrabromothymolphthaleinesulphonates exhibit a minimum water-solubility between pH 5.5 and 6.5. In fact, the above bases can be titrated with bromothymol blue in the presence of buffer mixtures with pH values lying within the above limits. The results are satisfactory; ephedrine shows a greater divergence from theory owing to its considerable water-solubility.

Procedure

0.2 ml of either an aqueous or chloroform solution of the base to be determined, are placed in a test-tube containing 2 ml of pH 5.5 buffer solution and 15 ml of chloroform. $1 \cdot 10^{-3} M$ bromothymol blue solution is run in with vigorous shaking of the mixture after each new addition of reagent. The BA compound, being thus extracted by the chloroform, imparts to the latter a bright yellow colour, whereas the water-phase, as far as the system contains an excess of organic base, remains colourless. The titration is interrupted as soon as a persistent yellowish shade is noticeable in the aqueous layer.

Besides bromothymol blue, we also employed several other indicators as titrants; *e.g.* quinine has been determined with bromophenol blue, strychnine with bromocresol green, *etc.*

This simple procedure is naturally of great interest especially for orientating purposes.

Indirect colorimetric method for the determination of alkaloids and other organic bases

As has been shown (p. 459), by adding an excess of an indicator acid to a suitably buffered solution containing an organic base, and by agitating the mixture with chloroform, the base is quantitatively extracted by the organic solvent as a coloured compound of the BA-type. Then, by separating the chloroform layer and decomposing the BA-compound by further shaking with a known volume of sodium hydroxide solution, we indirectly find out the required unknown base molarity by a colorimetric determination of the indicator, finally passing under its ionic form into the caustic solution*.

On applying this method the following points must be taken into consideration: *1. Suitable indicator concentration:* For optical reasons the dye concentration of the final aqueous extract at the very moment of the colorimetric estimation should be between $1.0 \cdot 10^{-5}$ and $2.5 \cdot 10^{-5}$. More intensely coloured solutions can of course be diluted so as to fall within these favourable concentration limits.

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* The dye extracted as BA by the chloroform could of course, be evaluated by comparing the colour intensity of the organic phase directly to a suitable standard scale. However, these solutions being generally of a yellow shade, are less appropriate for colorimetric work.

In order to avoid excessive dilutions, which would multiply any error introduced in matching colour, it is advisable to accept as a suitable initial indicator concentration in the aqueous phase that of $4 \cdot 10^{-4}$, as offering logical experimental conditions.
2. *Rational buffering*: Obviously, the aqueous phase must be buffered so as to exclude any possibility of traces of the available indicator excess to be extracted by the chloroform. This condition is adequately met in the case of a $4 \cdot 10^{-4} M$ bromothymol blue solution by working at pH 7.6, whereas the "safe" pH values for $4 \cdot 10^{-4} M$ solutions of bromocresol green, bromophenol blue and thymol blue are 6.6, 5.6 and 5 respectively.

Thus, by adding to the solution containing the base to be determined 0.4 ml of $5 \cdot 10^{-3} M$ indicator standard, by buffering at the above pH values and finally by bringing the volume of both phases to 5 ml, one is sure that no trace of free indicator acid can be extracted by the organic solvent, especially since, owing to the presence of the base, the final dye concentration in the water layer is always less than $4 \cdot 10^{-4}$.
3. *Base concentration limits.* We know that at the said minimum allowable pH values the base can be quantitatively extracted by the chloroform only if $[B]:[A] < 0.5$. Hence the base concentration (H_2O-phase) must never exceed $4 \cdot 10^{-4} : 2 = 2 \cdot 10^{-4}$. Of course, lower base concentrations are by no means detrimental. On the contrary they are desirable, especially in the case of relatively soluble organic bases.

We therefore must previously know the approximate base molarity of the sample in order to perform the determination under favourable concentration conditions. When nothing at all is known about $[B]$, the latter can easily be determined by the above titrimetric method.

Examples

Determination of procaine

As a first example of this application we give details of the technique we followed in studying the partition solubility of procaine (p. 459).

Procedure: 4.8 ml of the buffer chosen for each test were measured off in a small separator, 0.2 ml of $5 \cdot 10^{-3} M$ procaine hydrochloride solution plus 5 ml chloroform added and the mixture vigorously shaken for one minute.

Determination of the base dissolved in the chloroform layer

When both phases were limpid, the chloroform solution was quantitatively run off in a second separator, containing 0.4 ml of $5 \cdot 10^{-3} M$ bromothymol blue standard and 4.6 ml of pH 7.6 buffer solution. Then the mixture was vigorously agitated for one minute and the clear chloroform layer carefully transferred into a third separator. The aqueous solution of the second separator was washed out with 2-3 ml of pure chloroform and the washings, added to the main chloroform extract, further shaken with 10 ml of $0.1 N$ NaOH solution. After discarding the colourless solvent, the blue aqueous solution was suitably diluted (depending on its colour intensity) and the procaine content evaluated by obtaining a colour match with one of the standards (p. 458).

Determination of the base dissolved in the water layer

The initial aqueous extract which was abandoned into the first separator was rendered strongly alkaline by adding 0.5-1 ml of 10% caustic soda, the organic base was twice extracted with 5 ml of pure chloroform and the total chloroform extract further treated as above.

The technique followed in studying the influence of BTB on the partition solubility of procaine was quite similar except that in this series of experiments both reactants were determined in each layer.

Procedure: To 4.6 ml of the chosen buffer 0.2 ml of each $5 \cdot 10^{-3} M$ BTB and procaine hydrochloride solutions plus 5 ml of chloroform were added and the system thoroughly shaken for one minute. The chloroform layer was next treated in a second separator with the suitable volume of $1.0 N$ NaOH solution. The dye fixed by the alkali was then directly estimated as usual, whereas the liberated procaine base was determined by further treating the chloroform layer with an excess of BTB at pH 7.6 as already described. On the other hand, the dye and base concentration of the initial aqueous layer were determined by adding a measured volume of NaOH solution, by extracting the procaine with chloroform, and continuing as previously.

Determination of procaine hydrochloride in an injectable solution of magnesium thiosulphate

1. *Evaluation of the approximate molarity by a direct titration.* 0.1 ml of the sample was diluted with 2 ml of pH 5.4 buffer solution. By titrating in the presence of 10 ml chloroform, 1.75 ml of $1 \cdot 10^{-3} M$ BTB standard solution were consumed. Thus we found $1.75 \cdot 0.0002728 = 0.0004774$ g of procaine hydrochloride in 0.1 ml of liquid, a figure corresponding to the approximate molarity of $1.75 \cdot 10^{-2}$.

2. *Indirect accurate determination.* The liquid was diluted with an equal volume of distilled water. From this new solution, 0.1 ml was measured into a separator, 0.4 of $5 \cdot 10^{-3} M$ BTB standard (*i.e.* an excess of 114%), 4.5 ml of pH 7.6 buffer mixture and 5 ml of chloroform added, and the determination continued as already mentioned on p. 461. By diluting the final caustic extract to 40 ml and comparing the intensity of the colour to the standard scale, we found a BTB molarity of $2.25 \cdot 10^{-5}$. Hence the initial injectable solution contained:

$2.25 \times 40 \times 0.000002728 \times 2000 = 0.491$ of procaine hydrochloride per cent of liquid, *i.e.* 0.00982 g of this anaesthetic per 2 ml ampule (instead of the probable theoretical content of 0.01).

Determination of ephedrine in a potassium guaiacolsulphonate syrup

This dark-coloured preparation contained 6.5% of potassium guaiacolsulphonate, sugar, glycerine, etc., as well as 0.165% of ephedrine base as camphosulphonate.

1. *Direct orientating titration.* (1 ml of $1 \cdot 10^{-3} M$ BTB sol. = 0.00016523 g ephedrine alkaloid). 0.5 ml of $1 \cdot 10^{-3} M$ BTB standard were consumed by 2 ml of a solution, prepared by diluting 5.35 g of the syrup to 200 ml with distilled water. (Because of the yellow shade of the aqueous phase, due to the proper colour of the preparation, the titration was carried out at pH 7, in spite of the fact that at such a pH level lower results were to be expected. However, the end-point was easily perceivable by the appearance of a green colour in the aqueous layer.) Hence, the approximate molarity of our diluted solution was $0.25 \cdot 10^{-3}$, corresponding to a 0.1544% ephedrine content of the syrup.

2. *Indirect colorimetric determination.* 2 ml of the diluted liquid were brought into a small separator, 0.4 ml of $5 \cdot 10^{-3} M$ BTB solution (*i.e.* $[A]:[B] \cong 4$) and 2.6 ml of pH 7.6 buffer added and the mixture vigorously shaken for one minute with 5 ml of chloroform. The lower layer was quantitatively transferred into a second separator and the extracted ephedrine tetrabromothymolpthaleinesulphonate decomposed by treating the chloroform solution with $0.1 N$ NaOH. The total volume of the new aqueous layer brought finally to 40 ml had a colour concentration corresponding to a $1.33 \cdot 10^{-5}$ BTB-molarity. Consequently the syrup contained

$$\frac{0.00000165 \times 40 \times 1.33 \times 10000}{5.35} = 0.1655\% \text{ of ephedrine.}$$

Determination of strychnine in an injectable solution of strychnine sulphate, sodium glycerophosphate and sodium cacodylate

1. *Orientating titration* (1 ml $1 \cdot 10^{-3} M$ BTB = 0.0004285 g $(C_{21}H_{22}O_2N_2)_2H_2SO_4.5H_2O$). 2 ml of the sample, buffered at pH 7 required 2.1 ml of our $1 \cdot 10^{-3} M$ BTB standard. Therefore, the requested base concentration was $1 \cdot 10^{-3} \times 1.05$, corresponding to an approximate strychnine sulphate content of 0.04499%.

2. *Indirect colorimetric determination.* To 0.5 ml of the sample, diluted with 4.1 ml of pH 7.6 buffer, 0.4 ml of $5 \cdot 10^{-3} M$ BTB standard solution was added (*i.e.* four times as much dye as theoretically required), plus 5 ml chloroform. After final dilution of the caustic H_2O extract to 40 ml, its blue colour intensity was found to be equivalent to a BTB molarity ranging $1.48 \cdot 10^{-5}$. Consequently, each ml of injectable solution contained 0.504 mg of strychnine sulphate (stated content: 0.5 mg).

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Determination of amphetamine sulphate in a mixture of acetyl salicylic acid, caffeine and phenacetin

After weighing and powdering a number of tablets, mix an accurately weighed quantity of the homogeneous powder, equivalent to one tablet, with 10 ml distilled water, digest for 10 minutes with frequent stirring and filter or centrifuge. Transfer 1 ml of the clear liquid into a separator, containing 0.4 ml of $5 \cdot 10^{-3} M$ BTB standard solution, add some drops of $0.1 N$ NaOH solution until the indicator turns a distinct green, make up the volume to 5 ml by adding 3.6 ml of pH 7.6 buffer solution and shake the mixture with 5 ml chloroform for one minute. Treat the $CHCl_3$-extract with 40 ml of $0.1 N$ NaOH and compare the developed blue colour with the standard scale.

BTB molarity found $2 \cdot 10^{-5}$, corresponding to 0.003685 of amphetamine sulphate, *i.e.* $0.003685 \cdot 40 \cdot 10 : 1000 = 0.00147$ g of $(C_9H_{13}N)_2H_2SO_4$ in each tablet, instead of the stated amount of 0.0015.

By this method we successfully determined several other organic bases, using bromothymol blue as well as other indicator acids. Thus, quinine and strychnine have been accurately determined at pH 5.6 with bromophenol blue and at pH 3.2 with tropeolin OO, procaine, emetine, strychnine, quinine with thymol blue at pH 5, and so on.

The fact that we particularly occupied ourselves with bromothymol blue was not accidental. From another study dealing with the detection of alkaloids, (investigations in this connection are now in progress), we observed that generally speaking, this dyestuff yields $B\Delta$ compounds the water solubility of which is less than that of other indicator "$B\Delta$"-salts. On the other hand the colour strength and the relative stability of the alkaline BTB solutions against light are additional advantages indicating the use of this dye. Other indicators, as for example bromophenol blue, alizarinesulphonic acid *etc.*, which undergo a photochemical decomposition in an interval of only a few hours, are unsuitable as standards for colorimetric purposes. Of course, either a natural or artificial standard is superfluous when a photometer or spectrophotometer is used to match colours. The fact, however, that by using trivial means, an experienced worker may obtain equal precision with the unaided eye, encouraged us to avoid the use of optical apparatus, especially since the simplicity of the method would then have been lost.

It is superfluous to point out the multiple advantage offered by this colorimetric method, the simplicity of which helped us to bring about the quantitative study of solubilities, as summarized in the first part of this paper. The above examples merely illustrate its application in pharmaceutical analysis. However, the proposed technique is widespread in its applicability and should offer invaluable services in toxicological investigations and generally in those cases where the isolation of minute quantities of an alkaloid is practically impossible to attain and/or its determination problematic by routine methods.

Reviewing the biochemical literature we recently found that other investigators had already determined several alkaloids using methods based on a similar principle. PRUDHOMME[3] proposed the colorimetric determination of quinine in biological materials by treating the sample with eosin and by further extracting the coloured compound yielded with chloroform. BRODIE, UNDERFRIEND *et al.*[4] used methyl orange for the estimation of cinchona alkaloids and other organic bases in plasma and urine, by measuring the colour intensity of the resulting dichlorethylene extract. MARSHALL AND ROGERS[5] benefit by the property of bromothymol blue to yield with cinchona alkaloids colours extractable with benzene. SPINKS[6] suggested the use of eosin and a mixture of chloroform-butanol as the extractant for the fluori-

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metric evaluation of the drug "antrycide" in plasma. GETTLER AND SUNSHINE[7], modifying BRODIE AND UNDERFRIEND's method, suggest the use of chloroform instead of dichloroethylene for the extraction of the coloured compound, *etc.*

It must be noted that all these methods are rather complicated and of a restricted applicability.

SUMMARY

The influence of organic bases on the partition of bromothymol blue between water of varying H-ion concentration and chloroform was studied quantitatively. A principle for the accurate determination of minute quantities of organic bases by a colorimetric procedure has been established by this research and by the method developed the reverse influence could further be investigated. A number of analytical applications follow.

RÉSUMÉ

L'influence des bases organiques sur la répartition du bleu de bromothymol entre l'eau à différents pH et le chloroforme a été étudiée quantitativement. Ces essais ont permis d'établir une méthode de dosage colorimétrique pour de faibles quantités de bases organiques et d'examiner l'influence de l'indicateur sur le comportement des bases. La description d'un certain nombre d'applications analytiques complète cet exposé.

ZUSAMMENFASSUNG

Der Einfluss von organischen Basen auf die Verteilung von Bromthymolblau zwischen Wasser von verschiedenen pH-Werten und Chloroform wurde quantitativ untersucht. Diese Versuche erlauben eine kolorimetrische Bestimmungsmethode für kleine Mengen von organischen Basen aufzustellen und den Einfluss des Indikators auf das Verhalten der Basen zu prüfen. Die Beschreibung einer Anzahl analytischer Anwendungen vervollständigt diese Arbeit.

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QUADRIVALENT URANIUM AS A REDUCING AGENT IN POTENTIOMETRIC TITRATIONS

I. ESTIMATION OF FERRIC AND CERIC SALTS

by

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Quadrivalent uranium was first suggested by VORTMANN AND BINDER[1] as a reducing agent in volumetric analysis. Recently BELCHER, GIBBONS AND WEST[2] applied uranous solutions for the direct potentiometric titration of some oxidizing agents. These authors considered that although the reagent can be used for the direct titration of ferric iron and other oxidants the reactions are sluggish at room temperature. They increased the rate of the reaction by titrating at 60° C. In view of this they concluded that the reagent possesses no advantage over other reductants and in most cases is less convenient. However, in view of the tendency of certain oxidants to degrade at high temperatures, the reactions can be carried out more advantageously in the cold, if the optimum conditions of acidity are chosen and if certain catalysts are present in the reaction medium.

In the following experiments we applied quadrivalent uranium for the direct potentiometric titration of several oxidants at room temperature either alone or in the presence of each other, taking into account the changes in the redox potential of the U^{+6}/U^{+4} system with acidity, a factor of major importance in these titrations.

EXPERIMENTAL

I. Preparation of solutions

Quadrivalent uranium was prepared by the reduction of uranyl sulphate solutions containing $\sim$ 18 g UO_2SO_4 per litre and made 0.18 *N* with respect to H_2SO_4 or 1 *N* with respect to HCl, either electrolytically or in the Jones reductor using pure granulated zinc. For the electrolysis a cell was used similar to that previously described[3]. The electrolysis required a period of 2-4 h at a current density of 200-500 mA/cm². Under these conditions only U^{+4} was produced[4]. When zinc was used as the reductor care was taken to oxidize any U^{+3} formed, by bubbling air through the reduced solution for 5 minutes[5].

II. Standardization of the uranous solutions

The reducing power of the solutions prepared in H_2SO_4 were checked by $KMnO_4$ following the procedure recommended by EWING AND ELDRIDGE[6]. In the presence of HCl, the solutions were standardized with $K_2Cr_2O_7$ prepared according to the recommendation of FURNESS[7]. In all cases the end-points were determined potentiometrically.

III. Stability of the uranous solutions

According to MCCOY AND BUNZEL[8] the rate of oxidation of U^{+4} by atmospheric oxygen varies inversely with the square of the H^{+} ion concentration in the solution. GUSTAVSON AND KNUDSON[9]

inferred that in the presence of 30% H_2SO_4 the stability of U^{+4} was so great that it could be titrated in the presence of air. We extended these studies, taking into consideration the effect of other interfering factors. Samples of the solution in 0.1-18*N* H_2SO_4 were kept in loosely stoppered colourless or brown bottles or in the presence of metallic salts. The stability of the reagent was also studied, while bubbling air or oxygen at a rate of 200 bubbles per min through the solution. At suitable intervals samples were withdrawn by means of a pipette and titrated against standard $KMnO_4$.

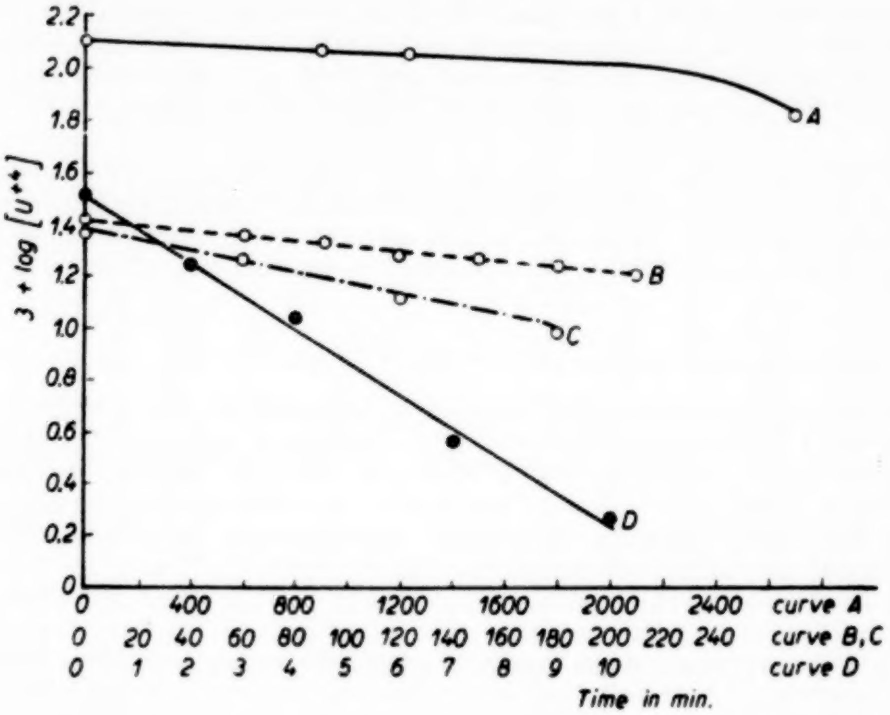

Fig. 1. (A) 0.125*N* U^{+4} in 5*N* H_2SO_4, exposure to atmospheric oxygen;
(B) 0.02118*N* U^{+4} in 3*N* H_2SO_4, bubbling air;
(C) 0.02250*N* U^{+4} in 5*N* H_2SO_4, in the presence of $KClO_4$;
(D) 0.03328*N* U^{+4} in 3*N* H_2SO_4, bubbling oxygen.

On plotting the logarithm of the U^{+4} concentration against time during exposure or while bubbling air or oxygen through, almost straight lines were obtained. By calculating the velocity constant of the reaction on the basis that it is one of first order, we obtained the *k* values recorded in Table I.

TABLE I

Normality of H_2SO_4	*Condition of the reaction*	*Original concentration of U^{+4}*	*Velocity constant k*
0.18	exposure to air in daylight	0.03375*N*	$1.67 \cdot 10^{-3}$
1	,,	0.03313*N*	$1.2 \cdot 10^{-3}$
1	exposure to air (dark bottle)	0.03375*N*	$6.39 \cdot 10^{-4}$
5	exposure to air in daylight	0.1250*N*	$2.5 \cdot 10^{-4}$
5	exposure to air + Co^{+2}	0.04563*N*	$9 \cdot 10^{-4}$
5	,, ,, ,, + Zn^{+2}	0.04063*N*	$1.39 \cdot 10^{-3}$
5	,, ,, ,, + H_3PO_4	0.02938*N*	$3.8 \cdot 10^{-4}$
5	,, ,, ,, + KCl	0.04188*N*	$6.1 \cdot 10^{-5}$
5	,, ,, ,, + $KClO_4$	0.02250*N*	$4.0 \cdot 10^{-3}$
3	bubbling air	0.02118*N*	$1 \cdot 10^{-3}$
1	,, ,,	0.02520*N*	$2.4 \cdot 10^{-3}$
3	,, oxygen	0.03328*N*	$2.9 \cdot 10^{-1}$
1	,, ,,	0.01875*N*	$3.5 \cdot 10^{-1}$

From these results the following conclusions could be drawn:

(i) *Effect of acid concentration.* The stability of the solutions increased with the rise of acidity as revealed by the decrease in the *k* values. However, in the presence of 10N H_2SO_4 an exceptional decrease in concentration was observed after 5 days which could not be attributed to oxidation but to the separation of green crystals of uranous sulphate. The same phenomenon occurred with 15 and 18N H_2SO_4 when separation of the solid took place after a shorter period.

(ii) *Effect of light.* In the absence of atmospheric oxygen light had no effect on the rate of oxidation, but in the presence of air the rate was greater in light than in the dark.

(iii) *Effect of salts.* KCl and HCl increased the stability of the reagent. Zn^{+2} and Co^{+2} salts, enhanced its oxidation while phosphoric acid was of little effect. $KClO_4$ increased the tendency of the solution towards oxidation and the rate of oxidation was comparable with that found when air was passed into the solution at a rate of 200 bubbles per minute.

IV. Solutions of the oxidants to be titrated, viz. ferricyanide, cupric copper, dichromate, permanganate, bromate, iodate and telluric acid were made from the AnalaR or purified products by dissolving them in distilled water. Ferric and ceric solutions were prepared by dissolution in 0.1N HCl and 2N H_2SO_4 respectively. These solutions were standardized according to recommended procedures[10].

V. The formal redox potential (E_f) *of the* U^{+6}/U^{+4} *system*

According to Luther and Michie[11] the redox potential of the U^{+6}/U^{+4} system increases with rise of the H+ ion concentration and with increasing ratio of (U^{+6}/U^{+4}). McCoy and Bunzel[8] measured the E_f value in 0.125N H_2SO_4 as 0.615 V, whereas Luther and Michie[12] gave 0.697 V. The E_0 value as calculated from measurements in that acid amounts to 0.419-0.404 volt[12]. Recently Belcher, Gibbons and West[2] measured the redox potential at different pH values (HCl medium) and obtained values varying between 0.2 V at pH = 1.5 to ∿ 0.500 V at pH = −1, which correspond to the acidity range ∿0.05N to ∿6N HCl. We extended our measurements to higher acidities both in the presence of HCl and H_2SO_4. This was done by directly measuring the potentials set when a bright platinum electrode was placed in a solution containing equimolecular quantities of U^{+6} and U^{+4} in the presence of 0.1 to 10N HCl and 0.1 to 15N H_2SO_4 against the saturated calomel as a reference half-cell. As is apparent from the curves shown in Fig. 2 the redox potential amounts to 0.3 volt in the 0.1N acid. On increasing the acidity of 1-7N HCl, E_f rises to 0.53 V within which acidity range it remains practically constant but increases again to 0.9 volt in the presence of 9N HCl. In the presence of H_2SO_4 the potential of the U^{+6}/U^{+4} system increases from ∿0.3 volt in 0.1N acid to 0.61 volt in 1-9N H_2SO_4 and increases thereafter to ∿1 volt. Both curves are similar to that of Belcher *et al.*[2] except above 7N HCl and 9N H_2SO_4.

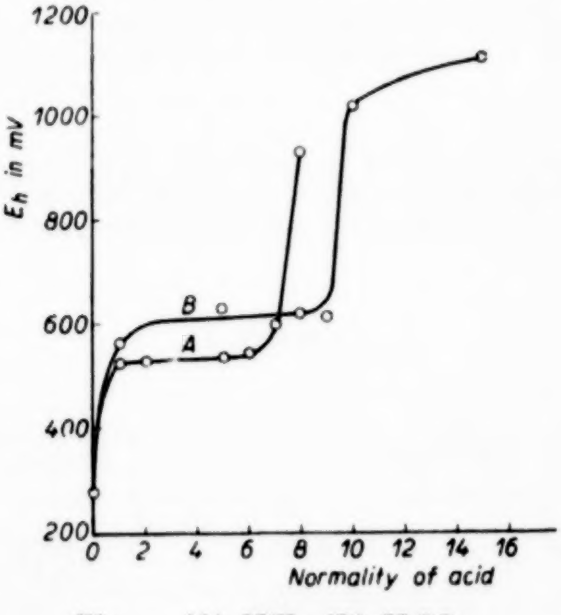

Fig. 2. (A) HCl; (B) H_2SO_4.

Estimation of ferric iron

Belcher, Gibbons and West[2] found that titration of ferric iron with quadrivalent uranium is troublesome even at 60° and they preferred slow titration in the cold. However, as may be

seen from the results shown in Table II reduction of ferric chloride with U^{+4} yields good results in 0.1-7*N* HCl. The end-points are attained with inflections amounting to 55-27 mV per 0.1 ml of U^{+4}. The inflection decreases with rise of acidity such that with 9*N* HCl no apparent inflection was observed. Reduction also proceeds to completion in the presence of 0.36-2.7*N* H_2SO_4. Ferric alum solutions could be titrated satisfactorily in the presence of 0.1*N* H_2SO_4, 0.5-3.3*N* HCl and 2.7*N* HNO_3.

TABLE II

Acidity	*Max. inflection per 0.1 ml U^{+4} mV*	*Equilibrium time at end-point min*	*Theoretical end-point ml*	*Exptl. end-point ml*	*Error %*
Titration of 5 ml 0.1408*N* $FeCl_3$ with 0.1389*N* U^{+4} solution					
Titration performed at 20° C					
0.1*N* HCl	43	5	5.07	5.09	+0.39
0.5*N* ,,	55	5	5.07	5.06	−0.19
3*N* ,,	47	8	5.07	5.08	+0.19
5*N* ,,	45	11	5.07	5.07	nil
7*N* ,,	27	14	5.07	5.06	−0.19
9*N* ,,	No characteristic inflection indicating end-point.				
Titration performed at 60° C					
5*N* HCl	27	1	5.07	5.05	−0.39
7*N* ,,	16	1	5.07	5.10	+0.59
Titration of 5.0 ml 0.1842*N* ferric ammonium sulphate with 0.1123*N* U^{+4} at 25° C					
1*N* H_2SO_4	77	1	8.20	8.16	−0.49
2*N* HCl	74	1	8.20	8.17	−0.37
2.7*N* HNO_3	72	5	8.20	8.15	−0.61

The reactions performed in the cold were found to take place rapidly at the beginning of the titration (needing ∿1 min) but they take 5-8 min at the end-point, provided that the acidity does not exceed 3*N*. With 5 and 7*N* HCl the time increases to 11 and 14 min respectively at the end-point. At 60° C the reaction is rapid even at the higher acidities.

The nonreducibility of ferric iron in 9*N* HCl is readily interpretable on the basis that the formal potential of the Fe^{+3}/Fe^{+2} couple in 8*N* HCl as given by CARTER AND CLEWS[13] (∿0.79 V) is less than that of the U^{+6}/U^{+4} system (∿ 0.9 volt) at the same acidity. At lower acidities the E_f values of the Fe^{+3}/Fe^{+2} system as computed from the titration curves amount to 0.675 V both in the presence of HCl and H_2SO_4, which value is comparable to that of SMITH AND RICHTER[14]. The proximity of the E_f values of the U^{+6}/U^{+4} and the Fe^{+3}/Fe^{+2} systems, although permitting reduction of Fe^{+3} with U^{+4} does not permit the appearance of considerable jumps at the end-point unless the acid concentration in solution is kept at ∿0.1*N*. Representative titration curves are shown in Fig. 3.

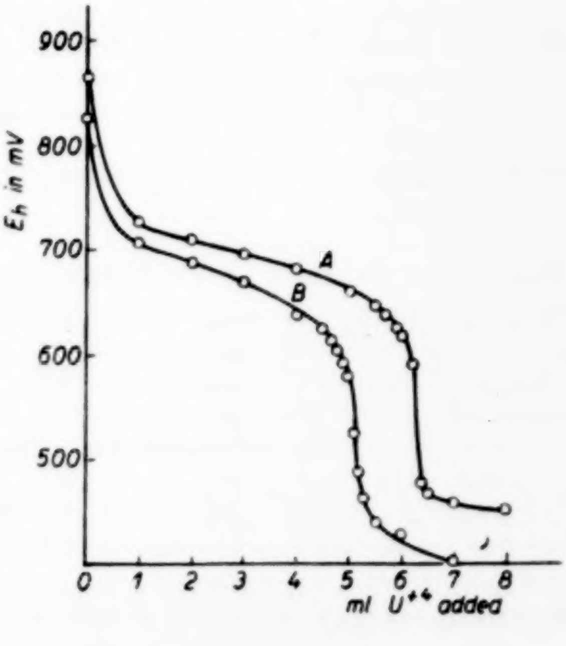

Fig. 3. (A) Titration of 10 ml 0.06446*N* Fe^{+3} in 0.1*N* H_2SO_4 with 0.102*N* U^{+4} (in 1*N* HCl);
(B) Titration of 5 ml 0.1408*N* Fe^{+3} in 0.5*N* HCl with 0.1389*N* U^{+4} (in 0.18*N* H_2SO_4).

Estimation of ferricyanide

The E_0 value for the ferro-ferricyanide couple amounting to 0.36 volt[15] does not permit the reduction of ferricyanide with U^{+4}. However, as may be visualized from the titration curves (Fig. 4), the formal potential amounts to 1 volt in 0.1*N* HCl and 1*N* H_2SO_4. This together with E_f U^{+6}/U^{+4} in 1*N* H_2SO_4 and 0.1*N* HCl = 0.6 volt and 0.3 volt corresponds to a degree of completion = $2.96 \cdot 10^{-5}$ and $1.23 \cdot 10^{-8}$ in both acids. This denotes a greater tendency for the complex ferricyanide to be reduced than the ferric ions. However, in contrast to Fe^{+3} the time necessary for the attainment of equilibrium is larger as was shown by BELCHER, GIBBONS AND WEST[2], varying from 10 min in 0.1*N* H_2SO_4 to 20 min in case of 0.1*N* HCl, to 60 min in 1*N* H_2SO_4 or 3*N* HCl.

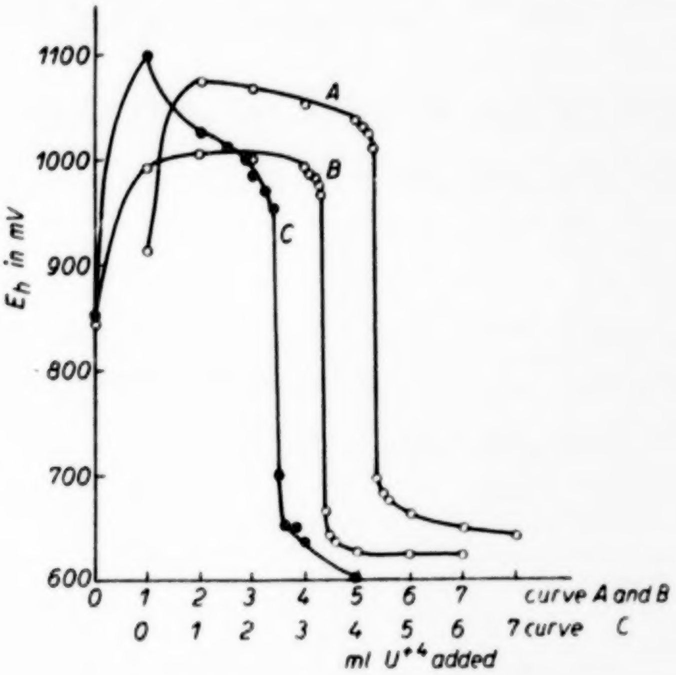

Fig. 4. Titration of 5 ml 0.1208*N* $K_3[Fe(CN)_6]$ with U^{+4}:
(A) in 0.1*N* HCl with 0.1389*N* U^{+4} at 25° C;
(B) in 1*N* H_2SO_4 with 0.1389*N* U^{+4} at 25° C;
(C) in 1.5*N* HCl with 0.1300*N* U^{+4} at 60° C.

The reaction is much accelerated on performing the titrations at 60° C when only 2-3 min are necessary, but then the errors are considerable. Even at that temperature, the time increases with rise of acidity to 7 and 12 min in 6*N* and 10*N* H_2SO_4 respectively. Good results are obtained when the titration is performed at room temperature. The reaction can be accelerated at the end-point by adding 2-3 drops of 0.1*N* ferric iron solution, in which case only one minute was found sufficient for equilibrium.

TABLE III

Acidity	*Max. inflection per 0.1 ml U^{+4} mV*	*Equilibrium time at end-point min*	*Theoretical end-point ml*	*Exptl. end-point ml*	*Error %*
Titration of 5.0 ml 0.1208*N* potassium ferricyanide with 0.1389*N* U^{+4} at 25° C					
0.1*N* H_2SO_4	130	10	4.35	4.37	+0.46
1*N* ,,	311	60	4.35	4.37	+0.46
0.1*N* HCl	322	20	4.35	4.34	−0.23
3*N* HCl	335	60	4.35	4.37	+0.46
6*N* HCl	160	60	5.95*	5.96	+0.17
Titration of 5.0 ml 0.1208*N* K-ferricyanide with 0.120*N* U^{+4} at 60° C					
0.1*N* H_2SO_4	229	3	5.03	2.86	−43.14
1*N* ,,	325	5	5.03	4.25	−15.51
4*N* ,,	280	2	5.03	4.32	−14.12
10*N* ,,	501	12	5.03	4.15	−17.49
16*N* ,,	No characteristic inflection indicating end-point				
0.5*N* HCl	254	3	5.03	3.48	−30.81
3*N* ,,	101	3	5.03	3.68	−26.84
7*N* ,,	134	5	5.03	4.32	−14.11

* U^{+4} = 0.1015*N*

References p. 473.

It should be noted that in the course of any titration, a yellowish precipitate is primarily formed which then passes through green to curdy white at the end-point. Such precipitations are possibly factors of major importance in causing the sluggishness of the reaction.

The titration curves in contrast to those of ferric iron are characterized by sharper inflections amounting to some hundreds of millivolts.

Estimation of ceric salts

The redox potential of the Ce^{+4}/Ce^{+3} system amounting to 1.61[15] volts is sufficiently high to permit the reduction of ceric salts by quadrivalent uranium. The equilibrium constant and the degree of completion of these reactions as calculated from the formal redox potentials of the systems concerned (computed from Fig. 5), *viz.* $E_f\ Ce^{+4}/Ce^{+3} = 1.4$ volt and $E_f\ U^{+6}/U^{+4} = 0.6$ volt in $1N\ H_2SO_4$, amount to $7.2 \cdot 10^{-27}$ and $9 \cdot 10^{-10}$ respectively. Reactions performed in presence presence of HCl are susceptible to considerable errors owing to the liberation of chlorine, but provided that the reactions are performed in the cold and the acid concentration does not exceed $6N$ HCl, good results could be obtained. Although the reaction is rapid at the beginning of the titration yet it needs ∿ 10 minutes at the end-point. It could be accelerated by the addition of ferric iron such that it takes only 3 minutes for the attainment of equilibrium. The time of reaction is also reduced by performing the titration at 60° C, when good results are obtained in solution containing up to $7N\ H_2SO_4$. At this temperature in the presence of HCl ($1N$ or above) and H_2SO_4 concentration greater than $7N$ the errors become considerable. The cold titration in the presence of the ferric iron catalyst is more advantageous.

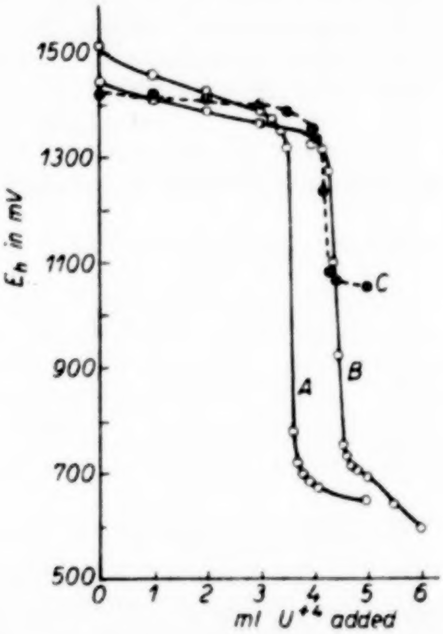

Fig. 5. Titration of 5 ml $0.0860N\ Ce^{+4}$ with U^{+4}:
(A) in $1N\ H_2SO_4$ with $0.1183N\ U^{+4}$ at 60° C;
(B) in $1N\ H_2SO_4$ with $0.0968N\ U^{+4}$ at 25° C;
(C) in $7N\ H_2SO_4$ with $0.1012N\ U^{+4}$ at 60° C.

As is apparent from Fig. 5, the titration curves are smooth with sharp inflections at the end-points.

Reduction of cupric copper

The redox potential of the Cu^{+2}/Cu^{+} couple amounts to 0.16 volt as compared with 0.46[15] volt for the system $Cu^{+2}/CuCl_2^-$. Both values are less positive to the formal potential of the U^{+6}/U^{+4} system in $1N$ acid and hence reduction of Cu^{+2} is not possible even when cuprous copper is complexed as $CuCl_2^-$. In conformity with this the titration curves are gradual without the appearance of an inflection characterizing the end-point.

Titration of ceric and ferric ions in a mixture of both

The redox potentials of the Ce^{+4}/Ce^{+3} and the Fe^{+3}/Fe^{+2} systems amounting to 1.61 and 0.771[15] are sufficiently widely separated from each other, thus permitting the reduction of both in two sharply-defined steps. The reaction occurs so rapidly in the presence of $0.36N\ H_2SO_4$

that it needs only 2 min at both end-points for the attainment of equilibrium. The inflections at the end-points amount to 428 and 60 mV at the ceric and ferric stages respectively (*cf.* Fig. 6, curve A). The experimental end-points coincide fairly well with the theoretically calculated values.

TABLE IV

Acidity		*Max. inflection per 0.1 ml U^{+4} mV*	*Equilibrium time at end-point min*	*Theoretical end-point ml*	*Exptl. end-point ml*	*Error %*
Titration of 5.0 ml 0.086*N* ceric sulphate with 0.0968*N* quadrivalent uranium at 25° C						
1*N*	H_2SO_4	349	10	4.44	4.43	−0.23
7*N*	,,	251	9	4.44	4.43	−0.23
11*N*	,,	181	9	4.44	4.43	−0.23
14.5*N*	,,	77	10	4.44	4.42	−0.45
1*N*	HCl	271	10	4.44	4.43	−0.22
3*N*	,,	261	10	4.44	4.44	nil
8*N*	,,	No characteristic inflection indicating end-points.				
Titration of 5.0 ml 0.086*N* ceric sulphate with 0.1204*N* U^{+4} at 60° C						
1*N*	H_2SO_4	533	3	4.20	4.17	−0.71
14.5*N*	,,	86	3	4.20	3.70	−11.91
3*N*	HCl	333	3	4.20	3.49	−16.90
1*N*	,,	462	3	4.20	4.1	−2.38

Titration of vanadate and ferric iron

Similar to the ceric-ferric mixture the vanadate-ferric mixture could be reduced by U^{+4} in two well-defined steps (Fig. 6, curve B). The redox potential of the V^{+5}/V^{+4} system is higher than the Fe^{+3}/Fe^{+2} system by 0.23 V, a difference which is sufficient for a successful titration. The experimental end-points coincide with the theoretical values. Although the inflection at the ferric stage did not differ from that of ferric in the ceric-ferric mixture or in pure ferric solution, the inflection at the vanadate is smaller than that of vanadate alone[16].

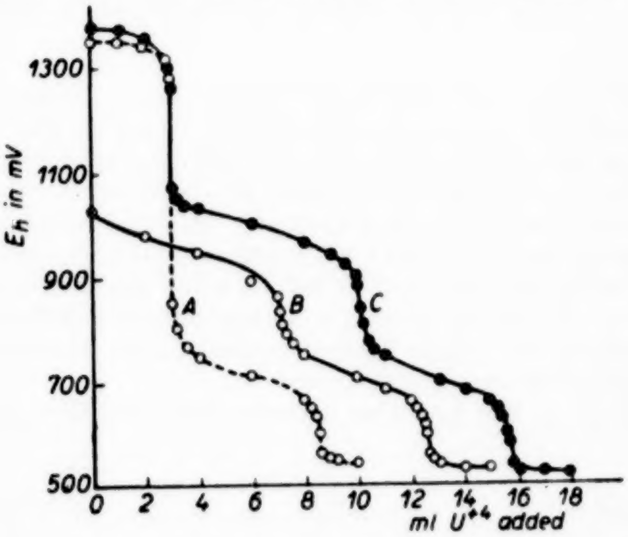

Fig. 6. (A) Titration of 5 ml 0.0481*N* Ce^{+4} + 5 ml 0.0859*N* Fe^{+3} with 0.0788*N* U^{+4}; (B) Titration of 5 ml 0.1083*N* V^{+5} + 5 ml 0.0874*N* Fe^{+3} with 0.0788*N* U^{+4}; (C) Titration of 5 ml 0.0481*N* Ce^{+4} + 5 ml 0.1083*N* V^{+5} + 5 ml 0.0874*N* Fe^{+3} with 0.0788*N* U^{+4}.

Titration of vanadate, ceric and ferric mixture

As may be seen from Fig. 6, curve C, the titration of this mixture with U^{+4} proceeds in 3 steps each characterized by a distinct inflection. At the ceric stage the inflection is sharper than the other two, amounting to 189 mV as compared with 35 and 49 mV at the vanadate and ferric stages.

The experimental results do not deviate considerably from the theoretical end-points, and the reaction proceeds rapidly.

The rapidity of the reactions in the above mixtures is due in part to the low acidities in which the titrations were performed ($0.36N$ H_2SO_4) and in part to the catalytic action of ferric iron.

ACKNOWLEDGEMENT

The authors wish to express their thanks to Prof. Dr. A. Riad Tourky for his interest in this work.

SUMMARY

Quadrivalent uranium is found to be a suitable reducing agent in potentiometric titrations, for the estimation of ferric and ceric salts. The stability of the reagent increases by raising the acidity and becomes considerable in the presence of HCl. The stability is not seriously affected by H_3PO_4 although Zn^{+2} and Co^{+2} ions enhance its oxidation. Light affects the stability of the reagent only in the presence of air.

The redox potential varies with acidity, being 0.3 volt at $0.1N$ HCl or H_2SO_4 rising to 0.53 or 0.61 in 1-$7N$ HCl or 1-$9N$ H_2SO_4 and increasing thereafter to $\sim$ 1 volt.

RÉSUMÉ

L'uranium(IV) peut être utilisé comme réducteur, pour le dosage potentiométrique des sels de fer(III) et de cérium(IV). La stabilité du réactif augmente avec l'acidité; elle est très grande en présence de HCl; elle n'est pas très influencée par H_3PO_4; par contre Zn^{+2} et Co^{+2} favorisent l'oxydation. Quant à l'influence de la lumière, elle ne se manifeste qu'en présence d'air. Le potentiel rédox varie avec l'acidité: 0.3 V pour HCl ou H_2SO_4 $0.1N$, 0.53 ou 0.61 V pour HCl 1 à $7N$ ou H_2SO_4 1 à $9N$ et environ 1 V pour des acidités supérieures.

ZUSAMMENFASSUNG

Uran(IV) kann für die potentiometrische Bestimmung von Eisen(III) und Cer(IV)-Salzen als Reduktionsmittel gebraucht werden. Die Haltbarkeit des Reagenzes verbessert sich mit ansteigender Säurekonzentration; sie ist sehr gross bei Anwesenheit von HCl, wird aber durch H_3PO_4 nur wenig beeinflusst. Dagegen begünstigen Zn^{+2}- und Co^{+2}-Ionen die Oxydation. Was den Einfluss des Lichtes betrifft, so ist dieser nur bei Gegenwart von Luft festzustellen. Das Redoxpotential verändert sich je nach der Säurekonzentration: 0.3 V für $0.1N$ HCl oder H_2SO_4, 0.53 V oder 0.61 V für 1 bis $7N$ HCl oder 1-$9N$ H_2SO_4 und ungefähr 1 V für höhere Säurekonzentrationen.

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QUADRIVALENT URANIUM AS A REDUCING AGENT IN POTENTIOMETRIC TITRATIONS

II. ESTIMATION OF DICHROMATE, PERMANGANATE, BROMATE AND TELLURATE

by

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In the previous paper we studied the reduction of ferric iron, ferricyanide and ceric salts with quadrivalent uranium either alone or in the presence of each other. In this paper we applied the reagent for the estimation of dichromate, permanganate, tellurate, and bromate ions separately or in a mixture containing them together with ferric and ceric salts.

EXPERIMENTAL

I. Estimation of dichromate

Belcher, Gibbons and West[1] studied the reduction of dichromate with U^{+4} and found that the reaction was sluggish at room temperature making the end-point rather indistinct, but when the titration was carried out at 60° C satisfactory and consistent results were obtained. We performed the titrations in the cold both in the presence of HCl and H_2SO_4 of various concentrations and in the presence of ferric iron as a catalyst. The reaction in the presence of $0.7N$ H_2SO_4 alone was rapid, needing only $\sim$ 2 minutes for the attainment of equilibrium at the end-point. However, the time increased with rise of acidity (see Table I) so that it takes at the end-point 5 min and 40 min in presence of $3.6N$ and $14N$ H_2SO_4 respectively. In the presence of HCl the reaction is

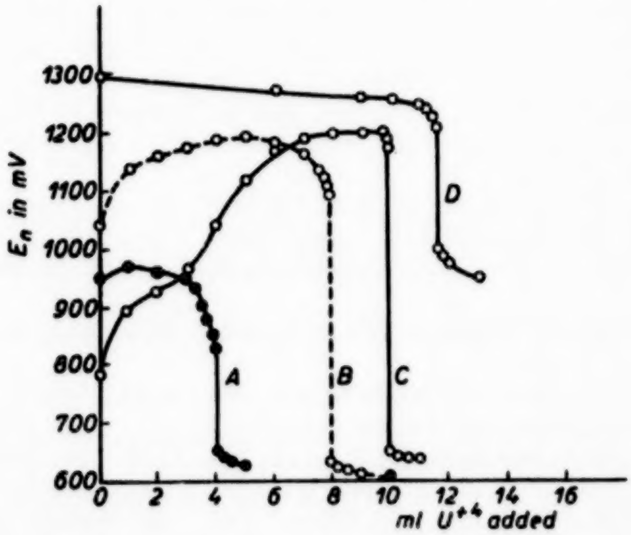

Fig. 1. Titration of $0.100N$ $K_2Cr_2O_7$ with U^{+4}
(A) 5 ml $K_2Cr_2O_7$ in $3.6N$ H_2SO_4 × $0.125N$ U^{+4} (in $0.36N$ H_2SO_4)
(B) 10 ml $K_2Cr_2O_7$ in $3.3N$ HCl × $0.125N$ U^{+4} (in $1N$ HCl)
(C) 10 ml $K_2Cr_2O_7$ (aqueous) × $0.100N$ U^{+4} (in $1N$ HCl)
(D) 4 ml $K_2Cr_2O_7$ in $20N$ H_2SO_4 × $0.03451N$ U^{+4} (in $0.36N$ H_2SO_4)

rapid only if the acidity is less than 2*N* when it takes $\sim$ 2 min at the end-point. The time increases to 5 and 10 min when the acid concentration is raised to 4 and 10*N* HCl respectively. However, in presence of few drops of ferric chloride the reaction velocity is increased at the higher acidities. The decrease in the reaction rate at higher acidities is apparently due to the rise in the E_f of the U^{+6}/U^{+4} system, which in 14*N* H_2SO_4 approaches the formal redox potential of the Cr^{+6}/Cr^{+3} couple ($\sim$ 1.1 volt).

Oxidation of U^{+4} with $Cr_2O_7^{-2}$ occurs rapidly in presence of 2.5-5*N* HCl and 3.6*N* H_2SO_4; the results are quite satisfactory. The degrees of completion of the reactions as calculated using the E_f value of the Cr^{+6}/Cr^{+3} system in 1-7*N* HCl or 2*N* H_2SO_4 as $\sim$ 1.11 volt and that of the U^{+6}/U^{+4} system as 0.53 and 0.6 volt in both acids, amount to $5 \cdot 10^{-14}$ and $4.3 \cdot 10^{-11}$ respectively.

Representative titration curves are shown in Fig. 1. Curve C represents the titration of neutral dichromate solution with U^{+4} (in 1*N* HCl). The curve exhibits an initial rise in potential due apparently to increase in the E_f value of the Cr^{+6}/Cr^{+3} system with rise of acidity. When the end-point is reached a sudden drop in potential occurs amounting to 400-500 mV. However, in the presence of an initial concentration of H_2SO_4 or HCl (curves A, B and D, Fig. 1) the rise in potential observed in the absence of acid decreased or disappeared completely.

TABLE I

Acidity	*Normality of U^{+4}*	*Max. inflection per 0.1 ml U^{+4} mV*	*Theoretical end-point ml*	*Exptl. end-point ml*	*Error %*
Titration of 0.1*N* $K_2Cr_2O_7$ with U^{+4}					
0.1*N* HCl	0.100*N*	532	10.0	9.95	−0.5
0.5*N* ,,	0.06667*N*	147	7.5	7.45	−0.66
1.4*N* ,,	0.1087*N*	106	4.6	4.63	+0.65
2.0*N* ,,	0.03379*N*	348	11.83	11.77	−0.52
4.0*N* ,,	0.03379*N*	928	11.83	11.92	+0.75
6.0*N* ,,	0.03379*N*	823	11.83	11.83	nil
0.7*N* H_2SO_4	0.03605*N*	462	13.87	13.83	−0.29
3.6*N* ,,	0.1670*N*	158	3.00	3.02	+0.67
7.2*N* ,,	0.03451*N*	464	11.59	11.57	−0.17
14.4*N* ,,	0.03451*N*	461	11.59	11.57	−0.17
21.9*N* ,,	0.03451*N*	447	11.59	11.53	−0.51

II. Titration of ceric, dichromate, vanadate and ferric solutions in presence of each other

(A) The redox potentials of the Ce^{+4}/Ce^{+3} and the Cr^{+6}/Cr^{+3} systems are not sufficiently removed from each other to permit the titration of the ceric and dichromate ions in two sharply separable steps. The formal redox potential of the Ce^{+4}/Ce^{+3} system in 1*N* HCl amounts to 1.34 volt as compared with 1.1 for the Cr^{+6}/Cr^{+3} at the same acidity.

Fig. 2, curve A, represents the titration of a solution having 0.0574 *N* Ce^{+4} and 0.100*N* Cr^{+6} content, titrated with 0.09250*N* U^{+4}, the reaction medium being approximately 1.5*N* HCl. The titration curve is characterized by a single steep inflection amounting to 460 millivolts per 0.1 ml reagent which corresponds to a total experimental end-point at 8.47 ml of U^{+4}, thus agreeing fairly well with the required value for the titration of both solutions (3.10 + 5.40 = 8.50 ml of reagent).

(B) Titration of dichromate and ferric solutions in the presence of each other, appears feasible as already reported by BELCHER, GIBBONS AND WEST[1]; because there is a sufficiently wide difference between their redox potentials at varying acidities amounting to 0.43 volt. Fig. 2, curve B shows a representative titration curve of a mixture containing 0.100*N* $K_2Cr_2O_7$ and 0.09971*N* $FeCl_3$ titrated with 0.1020*N* U^{+4} in the presence of 1*N* HCl. The curve is characterized by two inflections; the first amounting to 0.4 volt occurs 0.36% later than the end-point of the dichromate and the second amounting only to 52 mV occurs 0.2% later than the end-point of the ferric chloride. The same accuracy is encountered when the concentration one of the constituents is twice that of the other.

(C) Titration of dichromate and vanadate with 0.079 U^{+4} also gave rise to a curve with one single inflection corresponding to the reduction of both constituents, owing to the proximity of their redox potentials. The end-point differs only by 0.14% from the sum of the volume of U^{+4} equivalent to the constituents of the mixture.

References p. 481.

(D) In the titration of dichromate, vanadate and ferric mixture only Fe^{+3} could be titrated in a separate step. The two others are reduced simultaneously as in the mixture of dichromate and vanadate. The titration curve of the mixture is characterized by two inflections, the first corresponding to dichromate and vanadate and the other to the ferric solution. Both inflections coincide fairly well with the theoretical end-points.

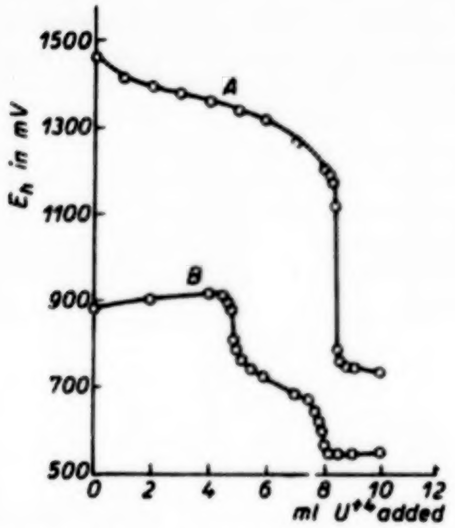

Fig. 2. (A) 5 ml 0.100N $K_2Cr_2O_7$ + 5 ml 0.0574N Ce^{+4} × 0.09259N U^{+4}
(B) 5 ml 0.06446N Fe^{+3} + 5 ml 0.100N $K_2Cr_2O_7$ × 0.1020N U^{+4}

III. Reduction of permanganate

(A) *In acid medium*

According to Ewing and Eldridge[2], the oxidation of U^{+4} is best performed in 2N H_2SO_4. We obtained good results also in the presence of 0.1-0.3N H_2SO_4 (see Table II). The titration curves are characterized by sharp inflections amounting to 300-400 mV and the end-points obtained potentiometrically do not deviate under these conditions from the visual ones.

TABLE II

TITRATION OF U^{+4} WITH $KMnO_4$

Acidity	*Max. inflection per 0.1 ml KMnO^4 mV*	*Normality of U^{+4}*	*Normality of $KMnO_4$*	*Theoretical end-point*	*Exptl. end-point*	*Error %*
0.1N H_2SO_4	415	0.1123	0.1422	7.9	7.88	−0.25
0.32N ,,	282	0.008886	0.01097	4.07	4.05	−0.5

Reduction of $KMnO_4$ was performed by Belcher, Gibbons and West[1] at 60° C. They avoided low results due to the presence of HCl by adding Zimmermann-Reinhardt solution. In this investigation we carried out the titrations in presence of H_2SO_4 in the cold. Reduction of aqueous $KMnO_4$ with U^{+4} (in 0.18N H_2SO_4) leads first to the separation of MnO_2; this then redissolves and undergoes further reduction to Mn^{+2}. The end-points are attained somewhat early due to incomplete reduction of the deposited MnO_2. Under these conditions the titration curve (Fig. 3) is characterized by two inflections, one (a) corresponding to the reduction of $KMnO_4$ to MnO_2 and the other (b) to the reduction of MnO_2 to Mn^{+2}. Curve B (Fig. 3) shows the course of the reaction, when at point b the solution is made 0.2N with respect to H_2SO_4.

Better results could be obtained in presence of an initial acidity of 0.1-0.56N H_2SO_4, provided that U^{+4} is not too dilute. In 0.7-2N H_2SO_4 the separation of MnO_2 is inhibited and the end-points coincide with the calculated values. At higher acidities than 3N H_2SO_4 the end-points are attained earlier than the theoretical values, and the errors increase with rise of acidity, owing apparently to loss of oxygen on decomposition. At such acidities the colour of $KMnO_4$ disappears before the potentiometric end-point is attained. The reaction velocity was found to vary appreciably with acidity. Thus, while it proceeds rapidly in 0.72N H_2SO_4, it takes 7-10 min in 1.4N H_2SO_4 and 20-30 min in 3.6N H_2SO_4 at the end-point. Although this time could be decreased to only 5 minutes by adding $Ni(NO_3)_2$ in the presence of 1.4N acid, the catalyst had but little effect at the higher acidities. However, ferric iron was found to enhance the reaction considerably at all acidities.

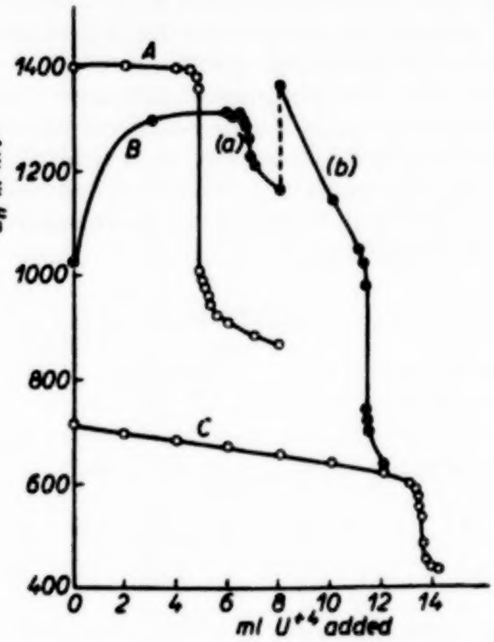

Fig. 3. (A) Titration of 5 ml 0.01097N $KMnO_4$ in 1.4N H_2SO_4 × 0.01133N U^{+4}
(B) Titration of 10 ml 0.1422N $KMnO_4$ × 0.1251N U^{+4}
(C) Titration of 25 ml 0.103N $KMnO_4$ in 2.5N NaOH × 0.1144N U^{+4} (in 0.2N H_2SO_4)

From the theoretical point of view, reduction of $KMnO_4$ with U^{+4} in acid medium is quantitative. The equilibrium constant and the degree of completion of the reaction as calculated using $E_f(U^{+6}/U^{+4})$ values as shown in Fig. 1 (Part 1) and the E_f MnO_4^-/Mn^{+2} values as computed from the titration curves, *viz.*

normality of H_2SO_4	0.1	0.5	1	4	8	12	N
E_f	1.35	1.40	1.42	1.42	1.42	1.45	volt

amount to $2.5 \cdot 10^{-136}$ and $4.3 \cdot 10^{-20}$ respectively at 1N H_2SO_4.

TABLE III

Acidity	*Normality of U^{+4}*	*Volume and normality of $KMnO_4$*	*Max. inflection per 0.1 ml U^{+4} mV*	*Theoretical end-point ml*	*Exptl. end-point ml*	*Error %*
0.1N H_2SO_4	0.1251	10 ml 0.1422	268	11.37	11.33	−0.34
0.72 ,,	0.0076	1 ,, 0.1009	261	13.33	13.33	nil
0.72 ,,	0.01133	5 ,, 0.01077	391	4.24	4.23	−0.21
1.44 ,,	0.00597	1 ,, 0.1009	277	16.90	16.93	+0.18
1.44 ,,	0.0156	2 ,, 0.1009	370	12.95	12.91	0.31
2.88 ,,	0.01589	5 ,, 0.01097	378	5.18	5.16	0.34
3.5 ,,	0.1237	5 ,, 0.1422	639	5.75	5.58	−2.96
7.2 ,,	0.02935	2 ,, 0.1009	638	7.4	6.3	−14.86
aqueous	0.1815	5 ,, 0.098	514	2.73	2.67	−2.2

(B) *In alkaline medium*

Reduction of $KMnO_4$ in alkaline medium yields MnO_4^{-2} which becomes further reduced to MnO_2. The reaction could be checked at the MnO_4^{-2} stage if the reducing power of the titrant is not very strong and if sufficient Ba^{+2} ions are present to precipitate $BaMnO_4$. This was not the case with U^{+4}, possibly owing to the strong reducing power of the reagent in the alkaline medium as suggested by BELCHER, GIBBONS AND WEST[1], the reaction always passing partially to MnO_2 as is apparent from the late end-points. Accordingly, the titration of $KMnO_4$ with U^{+4} was made in 1.5-3*N* NaOH in absence of Ba^{+2} ions, using uranous solutions containing little acid ($\sim$0.1*N*) and kept in a Zintl storage apparatus under CO_2. Reduction of MnO_4^- passed under these conditions completely to MnO_2, without the appearance of an inflection at the MnO_4^{-2} stage (curve C, Fig. 3).

The end-points are attended with reasonable inflections amounting to 50 mV and deviate but slightly from the calculated values. At alkalinities higher than 3*N*, although a small inflection appears at the manganate state, yet reduction always gives rise to the MnO_2 from the early stages. Under these latter conditions the end-points are attained earlier than the theoretical owing apparently to the autodecomposition of $KMnO_4$. Since no values are known for the E_f U^{+6}/U^{+4} couple in alkaline medium we calculated from free energy data[3], the value -0.16 volt for $E_{0(OH)}$ of the UO_3/UO_2 couple. This, together with $+0.588$ volt for the MnO_4/MnO_2 system, yield for K and a the values $5.2 \cdot 10^{-78}$ and $3.5 \cdot 10^{-16}$ which indicate a quantitative reaction between $KMnO_4$ and U^{+4} in alkaline medium (see Table IV)

TABLE IV

Alkalinity	*Max. inflection per 0.1 ml* U^{+4} *mV*	*Theoretical end-point ml*	*Exptl. end-point ml*	*Error %*
Titration of 10 ml 0.1422*N* $KMnO_4$ with 0.1055*N* U^{+4}				
1.5*N* NaOH	47	8.09	8.07	−0.24
2*N* ,,	47	8.09	8.08	−0.12
3*N* ,,	125	8.09	8.07	−0.24
Titration of 0.103*N* $KMnO_4$ with 0.1144*N* U^{+4}				
2.5*N* NaOH	51	13.5	13.55	+0.37

IV. Titration of permanganate in admixture with ferric, dichromate, vanadate and ceric ions

(A) The titration of $KMnO_4$ and Fe^{+3} was performed in the presence of 0.3*N* H_2SO_4 in order to avoid the action of HCl on permanganate. Owing to the great difference in the potential of the two systems, the mixture gives on titration two distinct separable inflections which occur in the region of the theoretical end-points (see Fig. 4, curve A). The equilibria were attained rapidly at the first inflection but needed 2-5 minutes for the attainment of equilibrium at the second end-point.

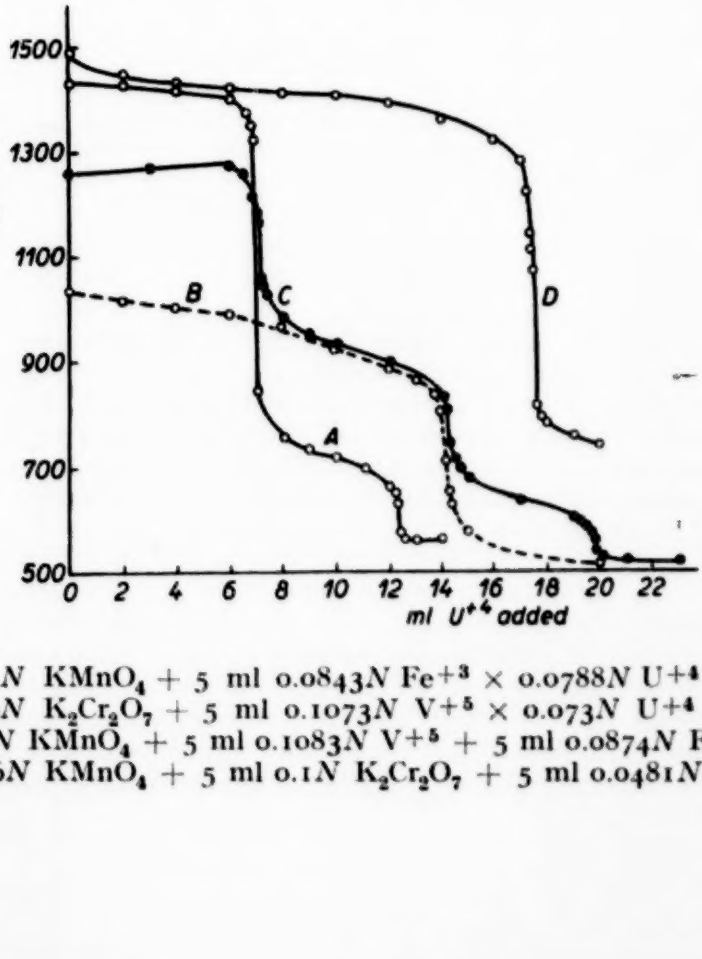

Fig. 4. (A) 5 ml 0.111*N* $KMnO_4$ + 5 ml 0.0843*N* Fe^{+3} × 0.0788*N* U^{+4}
(B) 5 ml 0.100*N* $K_2Cr_2O_7$ + 5 ml 0.1073*N* V^{+5} × 0.073*N* U^{+4}
(C) 5 ml 0.111*N* $KMnO_4$ + 5 ml 0.1083*N* V^{+5} + 5 ml 0.0874*N* Fe^{+3} × 0.07737*N* U^{+4}
(D) 5 ml 0.1066*N* $KMnO_4$ + 5 ml 0.1*N* $K_2Cr_2O_7$ + 5 ml 0.0481*N* Ce^{+4} × 0.073*N* U^{+4}

(B) Curve B Fig. 4 represents the titration of a mixture containing dichromate and vanadate with U^{+4}. Owing to the proximity of the formal redox potentials of the Cr^{+6}/Cr^{+3} system ($\sim$1.11 V) and the V^{+5}/V^{+4} ($\sim$1 V)[4], reduction of both constituents takes place at one step corresponding to the sum of the separate end-points.

(C) The mixture composed of $KMnO_4$, V^{+5} and Fe^{+3} gives rise to a titration curve characterized by 3 inflections (curve C, Fig. 4), the first amounting to 112 mV corresponds to the reduction of $KMnO_4$ and occurs 0.14% early, the second amounting to 59 mV corresponds to the reduction of V^{+5} and occurs 0.29% early, the third inflection amounting again to 18 mV is that of the Fe^{+3} and occurs 0.35% late. The end-points do not deviate appreciably from the theoretical end-points.

(D) The redox potentials of the MnO_4^-/Mn^{+2} and the Ce^{+4}/Ce^{+3} amounting to 1.52 and 1.61 volts are so close that titration of each constituent alone is not possible. The titration curve possesses only a single inflection amounting to 500 mV per 0.1 ml of U^{+4}. The experimental end-point coincides fairly well with the sum of the theoretical values. The ceric-permanganate-dichromate mixture gives on reduction a titration curve with one single inflection corresponding to the sum of the values of the U^{+4} solution equivalent to each constituent. Thus the experimental end-point of 17.45 ml 0.073*N* U^{+4} is $= 3.30 + 7.30 + 6.85$ ml 0.073*N* U^{+4} corresponding to 5 ml 0.0481*N* Ce^{+4}, 5 ml 0.1066*N* $KMnO_4$ and 5 ml 0.10*N* $K_2Cr_2O_7$.

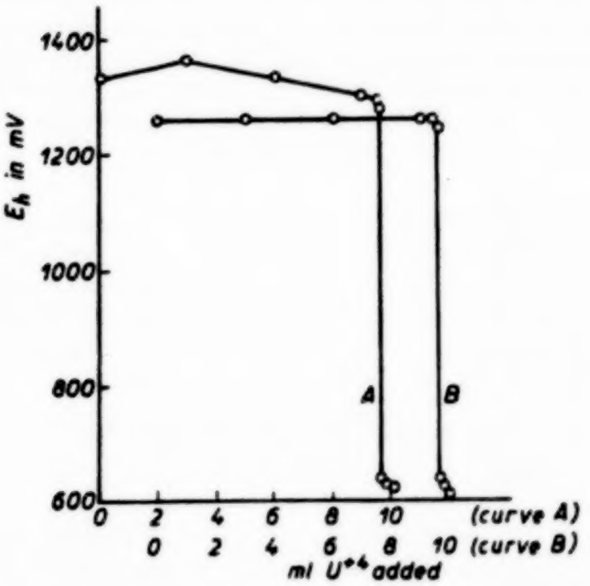

Fig. 5. Titration of 10 ml 0.100*N* $KBrO_3$ with 0.1030*N* U^{+4}
(A) in 3.3*N* H_2SO_4
(B) in 3.3*N* HCl

V. *Reduction of bromate*

In predicting the reducibility of bromate with U^{+4}, use was made of the redox potential of the system BrO_3^-/Br^- as calculated from free energy data amounting to 1.44 V[3]. The formal values as computed from the titration curves (Fig. 5) amount to 1.34-1.39 V in 2-6*N* H_2SO_4, 1.22-1.26 V in 2-4*N* HCl and 1.39 V in 4*N* HNO_3. These formal potentials together with the E_0 value of the BrO_3^-/Br^- system permit at the various acidities studied complete reduction of BrO_3^- with U^{+4}. The degrees of completion as calculated from these data and the potentials of U^{+6}/U^{+4} system amount to $2.3 \cdot 10^{-9}$ in 2*N* HCl and $3.9 \cdot 10^{-10}$ in 2*N* H_2SO_4. This is essentially confirmed by the results shown in Table V. The titration curves are smooth and characterized by sharp inflections at the end-points which are more pronounced at lower than higher acidities and in presence of H_2SO_4 and HCl than HNO_3.

As to the speed of the reaction under these conditions it was found that it takes place rapidly at the beginning of the titration but slows considerably at the end-point, needing 60 min. It could however be accelerated by adding few drops of a dilute ferric chloride solution, when only 15 minutes were found sufficient for the attainment of equilibrium. However, owing to the rapidity of the reaction at the beginning of the titration and the tendency of the potential to drift only at the end-point it is possible to trace the end of the reaction without awaiting the attainment of equilibrium.

TABLE V

Acidity	*Max. inflection per 0.1 ml U^{+4} mV*	*Theoretical end-point ml*	*Exptl. end-point ml*	*Error %*
Titration of 10 ml 0.0999N $KBrO_3$ with 0.103N U^{+4}				
5N HNO_3	249	9.70	9.67	−0.31
3.3N H_2SO_4	644	9.70	9.66	−0.41
8N ,,	249	9.70	9.66	−0.41
3.3N HCl	639	9.70	9.68	−0.21
6N ,, *	426	14.56	14.52	−0.27

* 15 ml BrO_3^- used.

VI. Titration of telluric acid

The redox potential of the Te^{+6}/Te^{+4} couple in acid solutions amounting to 1.02 volt[3] permits the reduction of Te^{+6} to Te^{+4}. However, as may be seen from the titration curves, the formal potential values amount to 0.550 volt which is not appreciably different from the E_f values of the U^{+6}/U^{+4} system at 1N acid. However, the titration could be successfully performed only at room temperature in presence of 0.1-4.5N H_2SO_4 or 0.1-0.5N HCl, since reactions performed at 60° C are associated with considerable errors. Under all conditions shown in Table VI the reaction takes from 5-10 min for the attainment of equilibrium.

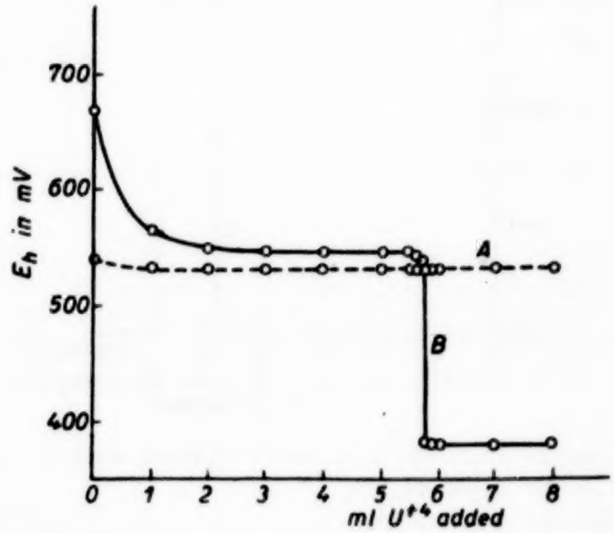

Fig. 6. Titration of 5 ml 0.07026N telluric acid with 0.0611N U^{+4}
(A) in 1N HCl
(B) in 0.1N H_2SO_4

TABLE VI

Acidity	*Max. inflection per 0.1 ml U^{+4} mV*	*Equilibrium time*	*Theoretical end-point ml*	*Exptl. end-point ml*	*Error %*
Titration of 5.0 ml 0.07026N telluric acid with 0.0611N U^{+4} at 25° C					
aqueous	66	20 min	5.75	5.75	nil
0.1N H_2SO_4	57	10 ,,	5.75	5.77	+0.35
4.5N ,,	19	5 ,,	5.75	5.74	−0.17
6N ,,	No inflection				
0.1N HCl	27	5 ,,	5.75	5.75	nil
0.5N ,,	42	10 ,,	5.75	5.75	,,
1N ,,	No inflection				
Titration of 5.0 ml 0.07026N telluric acid with 0.0911N U^{+4} at 60° C					
1N H_2SO_4	131	1 min	3.86	3.15	−18.39
6N ,,	25	10 ,,	3.86	4.05	+ 4.92

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SUMMARY

Quadrivalent uranium can further be used for the estimation of $K_2Cr_2O_7$, $KMnO_4$ (in acid or alkali), H_2TeO_4 and $KBrO_3$ either alone or in conjunction with Fe^{+3}, Ce^{+4} and V^{+5}. The reaction proceeds rapidly in dilute acid solutions and especially when Fe^{+3} iron is used as a catalyst. Reduction of aqueous $KMnO_4$ gives MnO_2 which then dissolves in the acid of the reagent and undergoes reduction to Mn^{+2}. In acid solutions no MnO_2 separates. In alkaline medium (1.5-3*N* NaOH) $KMnO_4$ is reduced absolutely to MnO_2.

RÉSUMÉ

L'uranium(IV) peut être utilisé pour le dosage de $K_2Cr_2O_7$, $KMnO_4$, H_2TeO_4 et $KBrO_3$, soit seuls, soit en présence de fer(III), de cérium(IV) et de vanadium(V). Ces réactions de réduction sont rapides, en solutions acides diluées, et surtout en présence de fer(III) comme catalyseur. La réduction de la solution aqueuse de $KMnO_4$ donne MnO_2; ce dernier se dissout ensuite dans l'acide et se réduit en Mn^{+2}. En solutions acides, on ne voit pas la formation de MnO_2, tandis qu'en milieu alcalin (NaOH, 1.5 à 3*N*), $KMnO_4$ se réduit quantitativement en MnO_2.

ZUSAMMENFASSUNG

Uran(IV) kann für die Bestimmung von $K_2Cr_2O_7$, $KMnO_4$, H_2TeO_4 und $KBrO_3$ allein oder in Gegenwart von Eisen(III), Cer(IV) oder Vanadin(V) angewendet werden. Diese Reduktionsreaktionen verlaufen in verdünnten Säurelösungen und vor allem bei Gegenwart von Eisen(III) als Katalysator schnell. Die Reduktion der wässrigen $KMnO_4$-Lösung ergibt MnO_2; letzteres löst sich nachher in der Säure und reduziert sich zu Mn^{+2}. In sauren Lösungen scheidet sich kein MnO_2 aus, während $KMnO_4$ in alkalischem Milieu (1.5 bis 3*N* NaOH) quantitativ zu MnO_2 reduziert wird.

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POLAROGRAPHIC HALF-WAVE POTENTIALS OF METAL IONS IN VARIOUS SUPPORTING ELECTROLYTES. I

by

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INTRODUCTION

In recent years it has become increasingly apparent that many polarographic investigations would be greatly facilitated by the availability of systematic data on the half-wave potentials, wave forms, reversibilities, *etc.*, of a large number of metal ions in various supporting electrolytes. The uses to which such data can be put, and the recent investigations in which they have been collected, have been summarized in an accompanying paper[1]. In this paper there are presented data concerning the polarographic characteristics of 28 metal ions in 9 supporting electrolytes. Two of these ($1M$ potassium thiocyanate and $0.1M$ pyridine-pyridinium chloride) have been studied, though less comprehensively, by various authors whose results have been tabulated elsewhere[4].

EXPERIMENTAL

All polarograms were recorded with a calibrated pen-and-ink recording polarograph[3]. A modified H-cell equipped with a sintered-Pyrex gas-dispersion cylinder to permit rapid deaeration[5] was used. Such cells are now available from E. H. Sargent and Co. (S-29438). The dropping mercury electrode assembly was entirely conventional.

Solutions were prepared from reagent grade chemicals, and were always 1 millimolar in the metal ion being studied, except for those containing thallium(I), which were always 0.2 millimolar. The alkaline pyrophosphate solution was freshly prepared every day or two to avoid ambiguities which might have resulted from extensive hydrolysis of the pyrophosphate. No maximum suppressor was used except where specifically noted.

The reliability of the data was ensured by frequent measurement of the half-wave potential of cadmium(II) in $0.1M$ potassium chloride. Whenever the measured value deviated by more than 2-3 millivolts from the accepted value, -0.578 volt *versus* S.C.E., the saturated calomel electrode and saturated potassium chloride – 4% agar bridge were replaced.

The measured half-wave potentials have been corrected both for the iR drop in the cell circuit and for the errors in the polarograph voltmeters.

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DATA AND DISCUSSION

The data secured are presented in Tables I-IX. Attention is directed to the following symbols: ">0" indicate that the wave merges with the anodic wave due to the dissolution of mercury or, in the ammoniacal and alkaline hydrazine media, with the anodic wave due to oxidation of the hydrazine. "NR" indicates that no wave, either cathodic or anodic, is observed. "W.-d." and "i.-d." mean well- and ill-defined, respectively, and refer to the precision which, in our opinion, could be achieved in the measurement of the wave height. Thus, a "very w.-.d." wave could be used as the basis of a very precise analytical method, whereas a "very i.-d." wave would be useless for analytical purposes, and in fact would probably render impossible the precise measurement of the diffusion current of a wave which followed it.

(Contribution No. 1325 from the Department of Chemistry of Yale University).

TABLE I

HALF-WAVE POTENTIALS IN 1*M* POTASSIUM THIOCYANATE

Element and oxidation state	*$E_{1/2}$ vs. S.C.E., volts*	*Oxidation state of product*	*Notes*
Ag(I)	>0	0	Small acute max., w.-d.
	−0.59		Very w.-d., $i = 1/4\ i_1$
	−1.14		Very irreversible, probably anomalous
Ag(I)^{a}	>0	0	Max. increased in height, very w.-d.
	−1.43		
	−1.63		Probably anomalous
As(III)^{b}	−0.68	0(film?)	Fairly w.-d., irreversible
	−1.09	−III(?)	I.-d., irreversible
	−1.56	?	Very i.-d.
As(III)^{a,b}	−0.70	0(film?)	W.-d., height halved by Triton
	−1.13		Fairly w.-d., very irreversible
	−1.61		I.-d., total wave height unchanged by Triton
As(V)	NR		
Bi(III)	>0	0	Fairly w.-d.
	−0.56		Small, w.-d.
Bi(III)^{b}	>0	0	Very w.-d.
Cd(II)	−0.651	0	Very small rounded max., fairly w.-d., reversible
	−1.27		Anomalous
Ce(IV)	−0.526	III(?)	Very w.-d., slightly irreversible
Co(II)	−1.084	0	Fairly i.-d., slightly irreversible
Cr(III)	−1.05	II	Fairly w.-d., very irreversible. May actually be poorly resolved double wave.
Cr(VI)	>0	?	Small, w.-d.
	−0.46	?	Very small, w.-d.
	−0.94	II	Main wave: fairly i.-d., irreversible
Cu(II)	>0	?	About one-fourth of total wave height; w.-d., diffusion-controlled
	−0.537	0	Acute max,. fairly w.-d., slightly irreversible
Cu(II)^{a}	>0	?	*Vide supra*
	−0.535	0	Very w.-d., slightly irreversible. Total wave height decreased *ca.* 10% by Triton

TABLE I (continued)

Element and oxidation state	*$E_{1/2}$ vs. S.C.E., volts*	*Oxidation state of product*	*Notes*
Fe(II)[c]	-1.5_2	0	I.-d.
Fe(III)[c]	>0	II	Fairly w.-d.; very w.-d. with 0.002% Triton X-100
H(I)	-1.55_3	0	W.-d., irreversible
In(III)	−0.717	?	Fairly w.-d. (plateau has appreciable negative slope), large rounded min. at −1.4 V, $E_{3/4}-E_{1/4}$ = −22 mV.
	−1.73	?	Fairly w.-d., height approx. equal to that of first wave, $E_{3/4}-E_{1/4}$ = −63 mV.
Mn(II)	−1.540	0	Fairly w.-d., nearly reversible
Mo(VI)	NR		
Ni(II)	−0.685	0	Fairly w.-d.; rounded max. at −1.0 V; nearly reversible
Pb(II)	−0.435	0	W.-d., reversible
	−1.33		Anomalous
Pb(II)[a]	−0.445	0	Very w.-d., reversible
Sb(III)[a]	>0	0	Very w.-d.
Sb(V)	NR		
Sn(II)	−0.46	0	Huge rounded max., very i.-d. Precipitation occurs on standing.
Sn(IV)[d]	−0.50	0(?)	Large rounded min. at −1.1 V, very i.-d.; practically unchanged by 0.002% Triton X-100
Te(VI)	−1.1	?	Small very i.-d. pre-wave
	−1.4	?	Fairly w.-d., irreversible
Te(VI)[a]	−1.10	?	Very small, fairly i.-d.
	−1.46	?	W.-d., irreversible
Tl(I)	−0.522	0	Fairly w.-d., reversible
	−1.07		Probably anomalous
U(VI)	−0.24	V	I.-d., reversible (?)
	−0.54	IV + V	W.-d.
	−1.21	IV	W.-d., very irreversible
U(VI)[a]	-0.26_0	V	Very w.-d., reversible
	−1.32	IV	Fairly w.-d., irreversible
V(IV)[e]	−1.11	II	Fairly i.-d., very irreversible
V(V)[e]	−0.62	IV	Fairly w.-d.
	−1.26	II	Fairly i.-d.
W(VI)[a]	NR		
Zn(II)	-1.05_5	0	Fairly w.-d., reversible, includes anomalous wave
Zn(II)[a]	-1.05_8	0	W.-d., reversible
	−1.55		Anomalous

[a]: With 0.002% Triton X-100
[b]: 0.001*M* hydrochloric acid present
[c]: 0.002*N* sulfuric acid present
[d]: 0.02*M* hydrochloric acid present
[e]: 1*M* ammonium acetate present

TABLE II

HALF-WAVE POTENTIALS IN 10*M* POTASSIUM THIOCYANATE

Element and oxidation state	*$E_{1/2}$ vs. S.C.E., volts*	*Oxidation state of product*	*Notes*
Ag(I)	>0	0	Small acute max., fairly w.-d.
As(III)[a]	−0.69	0(film?)	Small, w.-d., irreversible
	−1.50	−III(?)	Very w.-d., nearly reversible

TABLE II (continued)

Element and oxidation state	*$E_{1/2}$ vs. S.C.E., volts*	*Oxidation state of product*	*Notes*
As(V)	NR		
Bi(III)	>0	0	Fairly w.-d.; very w.-d. with 0.002% Triton X-100
Cd(II)	−0.778	0	W.-d., reversible
	−1.73		Probably anomalous
Ce(IV)	>0	III	Very w.-d.
Co(II)	−1.127	0	Very w.-d., irreversible
Cr(III)	-0.86_0	II	Fairly w.-d., irreversible
	-1.35_6	0(?)	I.-d., very irreversible
Cr(VI)	>0	?	Very i.-d.
	−0.6	?	Very w.-d.
	-0.96_3	?	Fairly i.-d., irreversible
Cu(II)	>0	I(?)	Fairly w.-d.
	−0.76	0(?)	Fairly i.-d., reversible (?)
	−1.21		Possibly anomalous
Cu(II)[b]	>0	I(?)	W.-d.
	−0.77	0(?)	Fairly w.-d., reversible (?)
	−1.28		Possibly anomalous
Fe(II)[c]	−1.41	0	Fairly w.-d., irreversible, preceded by hydrogen wave
Fe(III)[c]	>0	II	Very w.-d.
	−1.43	0	W.-d., very irreversible
H(I)	-1.13_2	0	W.-d., very irreversible
In(III)	-0.68_7	?	Fairly i.-d.: small min. at −1.0 V followed by very large min. at −1.5 V, $E_{3/4}$-$E_{1/4}$ = − 29 mV
Mn(II)	-1.63_0	0	I.-d., slightly irreversible
Mo(VI)	-1.51_7	?	Abnormally small, i.-d., irreversible
Ni(II)	-0.76_4	0	W.-d. except for large rounded max. at −1.2 V, nearly reversible
Pb(II)	−0.575	0	Small acute max., fairly i.-d., reversible
Pb(II)[b]	−0.575	0	Very w.-d., reversible
Sb(III)	>0	0	W.-d.
Sb(V)	NR		
Sn(II)	−0.56	0	Small max., i.-d., reversible
Sn(IV)[d]	−0.60	0(?)	Small, fairly w.-d., irreversible
Te(VI)	−1.04	?	Very small, fairly w.-d.
	−1.23	?	Small, very i.-d.
	−1.39	?	W.-d., irreversible
Tl(I)	−0.678	0	W.-d., reversible
	−1.25		Anomalous
Tl(I)[b]	−0.679	0	W.-d., reversible
	−1.39		Anomalous
U(VI)	>0	V(?)	Fairly i.-d., rounded max. at −1.05 V
V(IV)[e]	-1.00_4	II	W.-d., very irreversible
V(V)[e]	−0.71	IV	Two very i.-d. irreversible waves
	−1.02	II	
W(VI)	NR		
Zn(II)	-1.18_7	0	Very w.-d., reversible

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[a]: 0.001*M* hydrochloric acid present
[b]: With 0.002% Triton X-100
[c]: 0.002*M* sulfuric acid present
[d]: 0.02*M* hydrochloric acid present
[e]: 1*M* ammonium acetate present

TABLE III

HALF-WAVE POTENTIALS IN SATURATED HYDRAZINE DIHYDROCHLORIDE

Element and oxidation state	*$E_{1/2}$ vs. S.C.E., volts*	*Oxidation state of product*	*Notes*
Ag(I)	>0	0	Very w.-d.
As(III)	−0.192	0(film?)	W.-d., irreversible
	−0.575		Fairly w.-d., abnormally steep
As(V)	NR		
Bi(III)	−0.197	0	Very w.-d., reversible
Cd(II)	−0.729	0	Fairly w.-d., reversible
Ce(III)	NR		
Ce(IV)	—		Rapidly reduced to Ce(III), *q.v.*
Co(II)	NR		
Cr(III)	NR		
Cr(VI)	−0.590	III(?)	Fairly i.-d., irreversible
Cu(II)	>0	I	Very w.-d.
	−0.326	0	Very w.-d., reversible
Fe(II)	NR		
Fe(III)	>0	II	Very w.-d.
In(III)	−0.648	I(?)	W.-d., $E_{3/4}-E_{1/4} = -25$ mV
	-0.90_8	0(?)	Fairly w.-d., $E_{3/4}-E_{1/4} = -53$ mV, height = 1/3 that of total double wave
Mn(II)	NR		
Mo(V)	>0	IV	W.-d.
	−0.435	III	W.-d., irreversible
Mo(VI)	—		Rapidly reduced to Mo(V), *q.v.*
Ni(II)	NR		
Pb(II)	−0.544	0	Very w.-d., reversible
Sb(III)	−0.197	0	Very w.-d., nearly reversible
Sb(V)	>0	III	I.-d.
	−0.21	0	Very w.-d., irreversible
Sn(II)	−0.25		Small fairly w.-d. pre-wave
	-0.53_5	0	W.-d., reversible
Sn(IV)	−0.21	II	Very w.-d., irreversible
	-0.52_2	0	W.-d., reversible
Te(VI)	−0.747	?	Small w.-d. wave; final current rise begins abnormally early but no second plateau is observed
Tl(I)	−0.562	0	Very w.-d., reversible
U(VI)	-0.15_8	IV	Very w.-d.
	−0.885	III	W.-d.
V(IV)	−0.94	II	Large acute max., very i.-d., irreversible
V(IV)[a]	−0.99	II	Max. somewhat reduced, i.-d., irreversible
V(V)	−0.5	?	Small i.-d. pre-wave
	−0.9		Very i.-d., very irreversible
W(VI)	NR		Extensive pptn. of WO_3 from a 1 m*M* soln.
Zn(II)	-0.98_3	0	I.-d., reversible

[a]: With 0.002% Triton X-100

TABLE IV

HALF-WAVE POTENTIALS IN 1*M* HYDRAZINE — 1*M* AMMONIA — 1*M* AMMONIUM CHLORIDE

Element and oxidation state	$E_{1/2}$ *vs. S.C.E., volts*	*Oxidation state of product*	*Notes*
Ag(I)[a]	>0	0	Very w.-d.; i_d decreases on standing as Ag(I) is reduced by N_2H_4
As(III)	−1.11	0(film(?))	Small pre-wave
	-1.35_6	0(?)	Small max., fairly w.-d., irreversible. Final current rise (actually max. of next wave) begins about −1.5 V
As(III)[a]	−1.11	0(film(?))	Small pre-wave
	−1.30	0(?)	Large max., fairly w.-d., irreversible
	-1.56_5		Large max., irreversible
As(V)	NR		
Bi(III)[b]	−1.60	0	Very i.-d., irreversible
Bi(III)[a,b]	−1.54	0	I.-d., irreversible
Cd(II)	−0.823	0	Fairly i.-d., reversible
Cd(II)[a]	−0.842	0	Very w.-d., irreversible
	−1.56		I.-d., anomalous
Ce(III)	NR		
Ce(IV)	—		Rapidly reduced to Ce(III), *q.v.*
Co(II)	−1.29	0	Plateau very irregular, with series of alternating maxima and minima
Co(II)[a]	−1.285	0	Fairly w.-d., slightly irreversible
	−1.45		Fairly w.-d., probably anomalous
Cr(III)	−1.402	II	W.-d., reversible
	−1.7	0	Very i.-d. Soln. pink, slightly turbid
Cr(VI→III)	−1.400	II	Very w.-d., reversible
	−1.7	0	Very i.-d. Soln. pink, no visible ppt.
Cu(I)	−0.521	0	Fairly w.-d., reversible
Cu(II)	—		Rapidly reduced to Cu(I), *q.v.*
Fe(II)	-1.49_2	0	Large acute max., fairly w.-d.
Fe(II)[a]	-1.47_3	0	Fairly w.-d., slightly irreversible. No visible ppt.
Fe(III)[b]	-1.09_1	II	W.-d., irreversible
	-1.48_5	0	W.-d., slightly irreversible. i_2/i_1 = 4; probably partial reduction of Fe(III) by N_2H_4
In(III)[b]	-0.90_1	?	Fairly w.-d., irreversible
Mn(II)	-1.11_6	0	Acute max., fairly i.-d., probably slightly irreversible.
Mn(II)[a]	-1.11_6	0	Max. unchanged, fairly i.-d.
Mo(VI)	-1.71_8	V(?)	I.-d., $E_{3/4}$-$E_{1/4}$ = 45 mV
Ni(II)	-1.07_9	0	Large rounded max., fairly w.-d., reversible (?)
Ni(II)[a]	−1.06		Very i.-d., height approx. 1/3 that of total double wave
	−1.14	0	Very w.-d., irreversible, acute max. at −1.65 V
Pb(II)	−0.42		Small irreversible pre-wave
	−0.512	0	Fairly i.-d., reversible
Sb(III)	−0.742	0	Fairly w.-d., irreversible
	−1.6	?	Very i.-d.
Sb(V)	NR		
Sn(II)[b]	(−0.634)	IV	W.-d., irreversible
	−0.773	0	W.-d., reversible
	−1.62		I.-d., anomalous (?)

References p. 494.

TABLE IV (continued)

Element and oxidation state	*$E_{1/2}$ vs. S.C.E., volts*	*Oxidation state of product*	*Notes*
Sn(II)[a,b]	(−0.640)	IV	Very w.-d., irreversible
	−0.779	0	W.-d., reversible
	−1.62		I.-d., anomalous (?)
Sn(IV)	−1.13	II	Very i.-d., irreversible
	−1.35	0	Very i.-d., irreversible
Sn(IV)[a]	−1.26	II	I.-d., irreversible
	−1.57	0	I.-d., irreversible
Te(IV)	−0.714		Very w.-d. with characteristic large acute max. at −1.2 V., $E_{3/4}$-$E_{1/4}$ = −57 mV
Te(VI)	—		Rapidly reduced to Te(IV), *q.v.*
Tl(I)	−0.487	0	Fairly w.-d., reversible
U(VI)[b]	NR		
V(IV)	-1.20_9	III(?)	Fairly w.-d., irreversible
	−1.49	II(?)	I.-d., irreversible. Soln. becomes turbid yellow on standing; waves are abnormally small
V(V)	−1.146	?	Very w.-d., irreversible
W(VI)	NR		
Zn(II)	−1.330	0	Small acute max., fairly w.-d., reversible, includes contribution from anomalous wave
Zn(II)[a]	−1.330	0	W.-d., reversible
	−1.58		I.-d., anomalous

TABLE V

HALF-WAVE POTENTIALS IN 1*M* HYDRAZINE — 1*M* SODIUM HYDROXIDE

Element and oxidation state	*$E_{1/2}$ vs. S.C.E., volts*	*Oxidation state of product*	*Notes*
Ag(I)[a]	NR		
As(III)	NR		
As(V)	NR		
Bi(III)	−0.70	0	Very i.-d., slightly irreversible large rounded max. at −1.4 V
Bi(III)[b]	−0.705	0	Very w.-d., slightly irreversible
	−1.54		I.-d., irreversible, possibly anomalous
Cd(II)[a]	-0.70_1	0	Very i.-d., nearly reversible
	-0.81_3	0	W.-d., reversible
Ce(III)	NR		
Ce(IV)	—		Rapidly reduced to Ce(III), *q.v.*
Co(II)[a]	-1.42_3	0	W.-d., nearly reversible
Cr(III)	NR		
Cr(VI)	−0.93	III	Fairly w.-d., very irreversible
Cu(II)[a]	−0.8	?	Very small, i.-d.
Fe(II)	(−0.59)	III	Fairly w.-d., irreversible
	−1.38	0	I.-d., irreversible
Fe(III)[a]	−0.97	II	I.-d., irreversible
	−1.58	0	Fairly w.-d., slightly irreversible
In(III)	−1.15	?	I.-d., $E_{3/4}$-$E_{1/4}$ = −31 mV
	−1.30	?	Very i.-d., very irreversible, height = approx. 2/3 that of total double wave

References p. 494.

TABLE V (continued)

Element and oxidation state	*$E_{1/2}$ vs. S.C.E., volts*	*Oxidation state of product*	*Notes*
In(III)[b]	−1.20	?	Fairly w.-d., irreversible
	−1.54	?	I.-d., irreversible, height = approx. ½ that of total double wave
Mn(II)	NR		
Mo(VI)	NR		
Ni(II)	NR		
Pb(II)	-0.76_9	0	Fairly i.-d., irreversible, includes contribution from anomalous wave
Pb(II)[b]	−0.769	0	Very w.-d., reversible
	−1.58		Anomalous
Sb(III)	-1.20_7	0	W.-d., irreversible
Sb(V)	NR		
Sn(II)	(−0.873)	IV	Small max., fairly w.-d., slightly irreversible
	−1.219	0	Fairly w.-d., irreversible, includes contribution from anomalous wave
Sn(II)[b]	(−0.851)	IV	Very w.-d., slightly irreversible
	−1.219	0	Very w.-d., irreversible
	-1.57_2		Anomalous
Sn(IV)	NR		
Te(VI)	−1.4	?	I.-d., irreversible
Te(VI)[b]	−1.21	?	Fairly w.-d.; $E_{3/4}$-$E_{1/4}$ = −29 mV
Tl(I)	>0	0	Fairly i.-d.
U(VI)	-0.98_0	?	W.-d., irreversible
V(IV)	NR		
V(V)	NR		
W(VI)	NR		
Zn(II)	-1.52_5	0	Rounded max., fairly w.-d., slightly irreversible

[a]: Extensive precipitation from a 1 m*M* solution
[b]: With 0.002% Triton X-100

TABLE VI

HALF-WAVE POTENTIALS IN 10*M* SODIUM HYDROXIDE

Element and oxidation state	*$E_{1/2}$ vs. S.C.E., volts*	*Oxidation state of product*	*Notes*
Ag(I)[a]	>0	0	
As(III)	(−0.337)	V	Fairly w.-d., slightly irreversible
As(V)	NR		
Bi(III)	-0.74_3	0	Acute max., w.-d., slightly irreversible
Bi(III)[b]	-0.67_0	0	Very w.-d., nearly reversible
Cd(II)	−0.913	0	Large rounded max., fairly i.-d., reversible
Ce(IV)[a]	NR		
Co(II)	-1.58_4	0	Fairly w.-d., slightly irreversible
Cr(III)	−1.08	II	Very i.-d., irreversible
Cr(VI)	−0.837	III	Very w.-d., irreversible
Cu(II)	-0.55_3	0	Small max., fairly w.-d., slightly irreversible
Cu(II)[b]	-0.54_7	0	Max. greatly reduced, very w.-d., slightly irreversible
Fe(II)[a]	(-1.05_0)	III	Fairly w.-d., reversible
	-1.67_3	0	Fairly i.-d.

TABLE VI (continued)

Element and oxidation state	*$E_{1/2}$ vs. S.C.E., volts*	*Oxidation state of product*	*Notes*
Fe(III)[a]	−1.055	II	W.-d., reversible
In(III)	-1.38_2	?	Fairly w.-d., irreversible
Mn(II)[a]	(−0.477)	III(?)	Very w.-d., irreversible
Mo(VI)	NR		
Ni(II)	NR		
Pb(II)	-0.83_2	0	Acute max., w.-d., reversible
Pb(II)[b]	-0.82_5	0	Very w.-d., reversible
Sb(III)	(−0.573)	V	W.-d., slightly irreversible
	−1.246	0	Very w.-d., irreversible
Sb(V)	NR		
Sn(II)	(-1.14_4)	IV	Large max., w.-d., reversible
	-1.19_8	0	Large max., w.-d., reversible
Sn(IV)	NR		
Te(VI)	NR		
Tl(I)	−0.453	0	Fairly w.-d., reversible, rounded max. at −1.0 V
	−1.20		Probably anomalous
Tl(I)[b]	−0.458	0	Very w.-d., reversible
U(VI)[a]	-0.95_5	V(?)	W.-d., irreversible
V(IV)	(−0.558)	V	W.-d., slightly irreversible
V(V)	NR		
W(VI)	NR		
Zn(II)	-1.60_7	0	Fairly w.-d., slightly irreversible

[a]: Extensive precipitation from a 1 m*M* solution
[b]: With 0.002% Triton X-100

TABLE VII

HALF-WAVE POTENTIALS IN 0.1*M* PYRIDINE — 0.1*M* PYRIDINIUM CHLORIDE

Element and oxidation state	*$E_{1/2}$ vs. S.C.E., volts*	*Oxidation state of product*	*Notes*
Ag(I)	>0	0	I.-d.
As(III)	−0.90		I.-d., irreversible
	−1.05		I.-d., irreversible
As(V)	NR		
Bi(III)[a]	−1.00	0	I.-d., irreversible
Bi(III)[a,b]	−0.81		Small irreversible pre-wave
	−1.15		I.-d., irreversible
Cd(II)	−0.617	0	Very w.-d., reversible
Ce(IV)[a]	NR		Apparently complete pptn.
Co(II)	−1.050	0	I.-d.
Co(II)[b]	−1.050	0	Very w.-d., reversible (?)
Cr(III)	−0.986	II	Fairly i.-d., irreversible
Cr(VI)	>0	III	Large max., w.-d.
	−1.19	II	Fairly w.-d.
Cr(VI)[b]	>0	III	Max. incompletely suppressed, w.-d.
	−1.20	II	Fairly w.-d.
Cu(II)	>0	I	W.-d.
	−0.229	0	Large rounded max., fairly w.-d.
Cu(II)[b]	>0	I	W.-d.
	−0.219	0	Max. incompletely suppressed, w.-d.
Fe(II)	NR		
Fe(III)[a]	NR		Apparently complete pptn.
In(III)	NR		No visible pptn.

TABLE VII (continued)

Element and oxidation state	*$E_{1/2}$ vs. S.C.E., volts*	*Oxidation state of product*	*Notes*
Mn(II)	NR		
Mo(VI)	-0.237		Fairly w.-d. very small pre-wave
	-0.680	?	W.-d., irreversible
Ni(II)	-0.742		Acute max., fairly w.-d., reversible (?)
	-1.15_9		Irreversible, $i = 1/7\ i_1$
Ni(II)[b]	-0.751		Very w.-d., reversible (?)
	-1.16_5		W.-d., irreversible, $i = 1/7\ i_1$
Pb(II)	-0.398	0	W.-d., reversible
Sb(III)	-0.47_2		I.-d., irreversible
Sb(III)[b]	-0.57_4		I.-d., irreversible
	-0.75_2		Very w.-d., irreversible, $i = 2/3\ i_1$, total height unchanged by Triton
Sb(V)	NR		
Sn(II)[a]	-1.12	0	Fairly w.-d., irreversible
Sn(IV)	NR		
Te(VI)	NR		
Tl(I)	-0.451	0	Very w.-d., reversible
U(VI)	-0.22_8	V(?)	Fairly w.-d.
	-0.45_0	IV(?)	W.-d.
	-0.97_8	III(?)	Fairly w.-d., irreversible
V(IV)	-0.63	?	Very i.-d., irreversible
V(IV)[b]	-0.87_4	?	Fairly w.-d., irreversible
V(V)	-0.10_7	IV	Fairly w.-d., irreversible
	-0.43_1		W.-d., irreversible, $i = 1/2\ i_1$
	-0.77_2	II	W.-d., irreversible, $i = 3/2\ i_1$
W(VI)	NR		
Zn(II)	-1.032	0	Fairly w.-d., reversible

[a]: Extensive pptn. from a 1 m*M* solution
[b]: With 0.002% Triton X-100

TABLE VIII

HALF-WAVE POTENTIALS IN 1*M* PYRIDINE — 1*M* SODIUM HYDROXIDE

Element and oxidation state	*$E_{1/2}$ vs. S.C.E., volts*	*Oxidation state of product*	*Notes*
Ag(I)[a]	>0	0	Very i.-d.
As(III)	(-0.235)	V	Fairly w.-d., reversible
As(V)	NR		
Bi(III)[a]	-1.17_9	0	I.-d., irreversible
Cd(II)[a]	NR		Apparently complete pptn.
Ce(IV)[a]	NR		Large white ppt.
Co(II)[a]	-1.61	0	Fairly i.-d., irreversible, blue turbidity
Cr(III)	NR		
Cr(VI)	-1.46_7	III(?)	I.-d., very irreversible
Cr(VI)[b]	-1.47_6	III(?)	Fairly w.-d., very irreversible
Cu(II)[a]	-0.30_6		Small irreversible pre-wave
	-1.06		Max., very i.-d., irreversible
Cu(II)[a,b]	-0.93		I.-d., irreversible
Fe(II)	NR		
Fe(III)[a]	-0.56	II	W.-d., very irreversible
	-1.53	0	Fairly i.-d., irreversible
In(III)	NR		No visible pptn.
Mn(II)	-1.53		Small irreversible pre-wave
	-1.72	0	I.-d.

TABLE VIII continued)

Element and oxidation state	*$E_{1/2}$ vs. S.C.E., volts*	*Oxidation state of product*	*Notes*
Mo(VI)	NR		
Ni(II)	NR		No visible pptn.
Pb(II)	−0.83		Small pre-wave
	−1.15		Fairly i.-d., irreversible
Pb(II)[b]	−1.15		I.-d., irreversible
Sb(III)	(−0.232)	V	W.-d., reversible
Sb(V)	NR		
Sn(II)	(−0.483)	IV	Very w.-d., slightly irreversible
	−1.54		Small irreversible pre-wave
	−1.71	0	W.-d., abnormally high, probably includes contribution from anomalous wave
Sn(IV)	NR		
Te(VI)	NR		
Tl(I)	-0.48_9	0	Fairly i.-d., irreversible
U(VI)	−1.56		I.-d.
V(IV)	NR		
V(V)	NR		
W(VI)	NR		
Zn(II)	−1.724	0	Fairly w.-d., abnormally steep ($E_{3/4}$-$E_{1/4}$ = *ca.* 3 mV)

[a]: Extensive precipitation from a 1 m*M* solution
[b]: With 0.002% Triton X-100

TABLE IX

HALF-WAVE POTENTIALS IN 1*M* SODIUM HYDROXIDE — SATURATED SODIUM PYROPHOSPHATE

Element and oxidation state	*$E_{1/2}$ vs. S.C.E., volts*	*Oxidation state of product*	*Notes*
Ag(I)[a]	>0	0	Fairly w.-d.
	−0.97		Probably anomalous
As(III)[a]	NR		
As(V)	NR		
Bi(III)[a]	-0.68_1	0(?)	Fairly i.-d., irreversible
	−1.23	?	W.-d., irreversible, $i = 1/3\ i_1$
Bi(III)[a,b]	-0.68_8	0(?)	Very w.-d., slightly irreversible
	−1.46	?	I.-d., irreversible, $i = 1/5\ i_1$
	−1.67	?	Irreversible, $i = 1/2\ i_1$
Cd(II)[a]	-0.79_3	0	Fairly w.-d., reversible
Cd(II)[a,b]	-0.78_3	0	Fairly w.-d., slightly irreversible
	−1.58	?	I.-d., possibly anomalous, $i = 3\ i_1$
Ce(IV)[a]	NR		
Co(II)[a]	-1.45_4		Fairly w.-d., irreversible
	−1.82		I.-d., abnormally steep, $i = 1/5\ i_1$ Possibly two complexes in sluggish equilibrium
Co(II)[a,b]	-1.44_5		I.-d., irreversible, height decreased about 40% by Triton
	-1.60_4		W.-d., irreversible, $i = 4/5\ i_1$
	−1.79		I.-d., abnormally steep, $i = 1/10\ i_1$
Cr(III)[a(?)]	NR		
Cr(VI)	-0.82_1	III	I.-d., irreversible
	−1.04		W.-d., irreversible, possibly anomalous

TABLE IX (continued)

Element and oxidation state	*$E_{1/2}$ vs. S.C.E., volts*	*Oxidation state of product*	*Notes*
Cr(VI)[b]	-0.85_3	III	Very w.-d., irreversible, height decreased about 25% by Triton
	-1.44		Fairly w.-d., irreversible, possibly anomalous
	-1.65		
Cu(II)	-0.35_7	o(?)	I.-d., reversible probably two complexes in sluggish equilibrium
	-0.44_0	o(?)	Small max., w.-d.
	-1.09		W.-d., probably anomalous
Cu(II)[b]	-0.35_5	o(?)	I.-d., reversible *vide supra*
	-0.44_0	o(?)	Very w.-d., nearly reversible
	-1.39		Small, i.-d., probably anomalous
	-1.65		
Fe(II)	NR		
Fe(III)[a]	-0.96_8	II	Fairly w.-d., irreversible
	-1.55_9	o	Fairly w.-d., nearly reversible, $i < 2\, i_1$
Fe(III)[a,b]	-0.93_6	II	Very w.-d., irreversible
	-1.54_6	o	I.-d., slightly irreversible, $i > 2\, i_1$
In(III)[a]	-1.12		I.-d., irreversible
	-1.28		Fairly w.-d., irreversible, $i = 3/4\, i_1$
In(III)[a,b]	-1.13_0	?	W.-d., $E_{3/4}$-$E_{1/4}$ = −57 mV
	-1.58_8	?	W.-d., irreversible, $i = 2i_1$
Mn(II)[a]	-0.77		I.-d. Two irreversible prewaves of equal height, possibly due to Mn(III) formed (?)
	-0.96		Very w.-d.
	-1.71_1	o	Fairly w.-d., reversible
Mo(VI)	NR		
Ni(II)[a]	NR		
Pb(II)	-0.763	o	Fairly w.-d., reversible
	-1.14		Very i.-d., probably anomalous, $i = i_1$
Pb(II)[b]	-0.758	o	Very w.-d., reversible, height decreased about 20% by Triton
	-1.55		I.-d., probably anomalous, $i = 1/2i_1$
Sb(III)	(-0.452)	V	Small max., w.-d., reversible
	-1.194	o	Fairly i.-d., irreversible, includes contribution from anomalous wave
Sb(III)[b]	(-0.439)	V	Very w.-d., slightly irreversible
	-1.194	o	Fairly i.-d., irreversible, contribution from anomalous wave reduced but not eliminated
Sb(V)	NR		
Sn(II)	(-0.89)	IV	Large max., w.-d.
	-1.16	o	Small max., fairly i.-d., includes contribution from anomalous wave
Sn(II)[b]	(-0.84)	IV	Very w.-d., irreversible
	-1.17	o	W.-d., irreversible
	-1.64		W.-d., anomalous
Sn(IV)	NR		
Te(VI)	-1.54_0		Large acute max., i.-d., irreversible
Te(VI)[b]	-1.56_1		Max. greatly reduced, i.-d., irreversible
Tl(I)[a]	-0.510	o	Fairly w.-d., reversible
	-1.21		I.-d., probably anomalous, $i = 2\, i_1$
U(VI)[a]	-0.92_6	IV(?)	I.-d., $E_{3/4}$-$E_{1/4}$ = −63 mV
	-1.12_3	III(?)	Fairly w.-d., irreversible, $i = 1/2\, i_1$

TABLE IX (continued)

Element and oxidation state	*$E_{1/2}$ vs. S.C.E., volts*	*Oxidation state of product*	*Notes*
V(IV)	(−0.438)	V	Very w.-d., reversible
V(V)	NR		
W(VI)	NR		
Zn(II)	-1.50_2	0	I.-d., irreversible
	-1.73_7		Fairly w.-d., irreversible, $i = 1/5\, i_1$
Zn(II)[b]	-1.50_2	0	Very i.-d., irreversible
	-1.71_8		Fairly w.-d., irreversible, $i = 3/4\, i_1$

[a]: Extensive precipitation from a 1 m*M* solution
[b]: With 0.002% Triton X-100

SUMMARY

Data on the polarographic half-wave potentials, wave characteristics, probable reduction products and other polarographically important information are tabulated for 28 metal ions in 9 supporting electrolytes containing hydrazine, pyridine, sodium hydroxide, potassium thiocyanate, and pyrophosphate.

RÉSUMÉ

Des tables de potentiels de demi-vagues polarographiques, de caractéristiques de sauts, de produits de réduction probables et d'autres renseignements polarographiques importants sont données pour 28 cations dans 9 électrolytes de base, renfermant de l'hydrazine, de la pyridine, de l'hydroxyde de sodium, du thiocyanate de potassium et du pyrophosphate.

ZUSAMMENFASSUNG

Es werden Tabellen gegeben mit polarographischen Halbwerts-Potentialen, Eigenschaften der Sprünge, wahrscheinlichen Reduktionsprodukten und mit anderen wichtigen polarographischen Auskünften für 28 Kationen in 9 Grund-Elektrolyten, welche Hydrazin, Pyridin, Natriumhydroxyd, Kaliumthiocyanat und Pyrophosphat enthalten.

REFERENCES

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Received August 6th, 1955

BOOK REVIEW

Hefe und Alkohol sowie andere Gärungsprodukte, H. KRETZSCHMAR, Springer-Verlag, Berlin-Göttingen-Heidelberg 1955. XV + 648 pages, 176 illustrations, 3 diagrams. Price DM 66.—.

This thorough and comprehensive textbook on fermentation technology not only discusses the preparation of yeast, alcohol and yeast products, but also the preparation of other products using micro-organisms. In this connection mention can be made of the preparation of lactic acid, acetic acid, citric acid, acetone and a number of other compounds with special fermentation methods and the preparations of vitamins, dextran and antibiotics the development of which owes much to the experience of fermentation experts.

Analysts will be particularly interested in the section on analytical methods for molasses, yeast, alcohol etc., which comprise approximately one tenth of the book. The author in the rest of the book has described the many variations of the preparative methods but for the analytical section he has chosen to describe certain selected methods. Some of the methods are well-known, others are based on well-known principles, but the comprehensive description of the details of the methods shows a thorough investigation. However, the section on vitamin determinations is incomplete and cannot be substituted for the special books on this subject. The description of the tests which are so important for judging the quality of alcohol, namely, taste and smell is too brief. No mention is made of the technique of the tests or of the statistical evaluation of the results.

F. REIMERS (Copenhagen)

REVUES DE LIVRES

Chemical and Spectrographic Analysis of Magnesium and its Alloys, par A. MAYER et W. J. PRICE, Magnesium Elektron Ltd., Manchester, 1955, 248 p., 25 fig.; prix: 3 guineas.

Dans ce livre les auteurs ont rassemblé les méthodes d'analyse du magnésium et de ses alliages, recommandées par Magnesium Elektron Ltd. Ils n'ont pas la prétention de nous présenter „la meilleure méthode" pour le dosage de chaque élément, mais des méthodes qui, essayées pendant de longues périodes dans les laboratoires de Magnesium Elektron Ltd., ont donné des résultats très satisfaisants, et peuvent être considérées comme méthodes recommandables, directement applicables dans presque tous les cas qui peuvent se présenter.

La première partie est consacrée aux méthodes chimiques et physico-chimiques. Tous les éléments rencontrés à l'heure actuelle dans le magnésium et ses alliages y sont traités, par ordre alphabétique. La description des méthodes est remarquablement claire et complète. Une discussion élémentaire des principes théoriques qui sont à la base de chaque méthode décrite en permet l'application consciencieuse même pour des analystes ou des assistants non routinés.

La seconde partie du travail traite spécialement le dosage des différents éléments par analyse spectrographique. Après un aperçu des méthodes décrites dans la littérature, on y trouve un exposé bref des principes de la spectrographie, suivi de la description des méthodes employées par Magnesium Elektron Ltd. On pourrait regretter que la Firme n'ait pas encore appliqué jusqu'ici la méthode d'analyse directe, dont les données pratiques seraient très intéressantes.

La valeur du livre est augmentée du fait qu'il a été conçu dans le but de pouvoir le compléter, au fur et à mesure qu'elles apparaissent, par de nouvelles méthodes, plus exactes ou plus rapides, et par la description de méthodes d'analyse pour des éléments dont le dosage pourrait se justifier dans l'avenir.

Le livre est vivement recommandé à tous ceux qui sont intéressés à l'analyse du magnésium et de ses alliages.

J. EECKHOUT (Gand)

Polarographic Techniques, par L. MEITES, Interscience Publishers, Inc., New York, 1955, 317 pages, 44 fig., prix: $ 6.00.

Le Professeur MEITES, bien connu pour ses travaux en polarographie, vient de faire paraître un ouvrage qui rendra de précieux services à tous ceux qui utilisent cette méthode.

On y trouve la description détaillée de la technique opératoire de la polarographie. L'auteur traite de l'appareillage et plus particulièrement des cellules, du capillaire et des électrodes de référence. Un chapitre est consacré à l'étude des courants résiduels, du courant de migration et des courants d'ordre catalytique. Un autre renferme la théorie de la courbe potentiel-courant. Plus loin, l'auteur examine la question du potentiel de demi-vagues et de son interprétation. Les chapitres suivants s'intitulent: maxima et leur élimination, technique de l'analyse polarographique quantitative, titration ampérométrique et techniques spéciales.

Cet ouvrage est fort bien présenté, la lecture en est aisée et l'exposé fort clair. A la fin de chaque chapitre, le lecteur trouvera, heureuse innovation, une série d'expériences pratiques minutieusement décrites et qui lui permettra d'acquérir une maîtrise parfaite de la technique polarographique.

A la fin du livre, l'auteur étudie les perturbations provenant du circuit polarographique. Il donne onze courbes potentiel-courant présentant des anomalies et dans chaque cas, il en donne l'origine et les moyens de les corriger.

Excellent ouvrage que nous recommandons vivement à tous ceux — et ils sont de plus en plus nombreux — qui utilisent cette élégante méthode.

D. MONNIER (Genève)

Traité de Micro-analyse Minérale, par CLÉMENT DUVAL, Presses Scientifiques Internationales, Paris, 1955, Tome II, 448 pages, 59 figures, prix: f. frs. 3000.

Respectant l'horaire qu'il s'était proposé, le Professeur CLÉMENT DUVAL vient de faire paraître le Tome II de son traité de micro-analyse minérale.

Nous ne pouvons que répéter ici ce que nous avons dit lors de la parution du Tome premier. La bibliographie est très importante et s'étend jusqu'à fin 1954, début 1955; chaque référence a été minutieusement choisie; une présentation impeccable malgré le prix modique de l'ouvrage; un texte clair et dépouillé.

Ce deuxième Tome a pour objet les groupes III A, IV A, V A, VI A et VII A. En outre, le lecteur trouvera des renseignements fort substantiels ainsi qu'une bibliographie succincte des éléments transuraniens.

Ce livre apporte aux chimistes une documentation de premier ordre; les méthodes classiques voisinent avec les procédés les plus modernes de l'analyse physico-chimique, avec la polarographie, colorimétrie, coulométrie, potentiométrie etc.

Nous sommes certains que le succès de cet ouvrage s'affirmera de plus en plus.

D. MONNIER (Genève)

SIMPLE INSTRUMENT FOR TITRIMETRY WITHOUT VISUAL INDICATORS. GASOMETRIC TITRATIONS

XII. ARGENTOMETRY

by

OTTO RICHARD GOTTLIEB

Instituto de Química Agrícola, Ministério da Agricultura, Rio de Janeiro (Brazil)

The present communication has two purposes. The first is to show that the gasometric titration method can be used not only for acid-base and redox reactions (as already reported in previous papers[1]), but also for precipitation and complex-formation reactions. The second is to describe an improved model of the titration apparatus (Fig. 1).

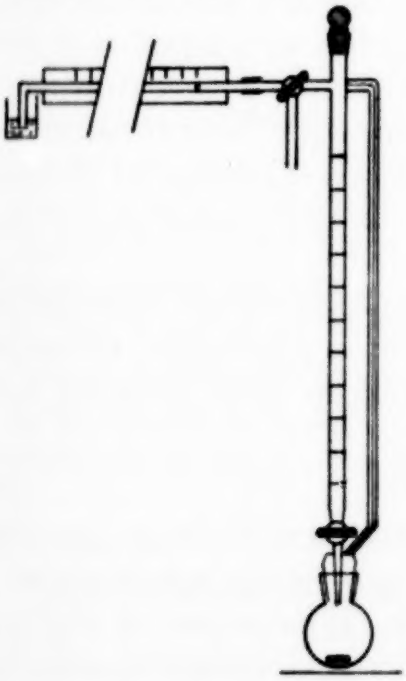

Fig. 1. Improved model of titration apparatus.

DESCRIPTION OF INSTRUMENT

The titration vessel is a 50 ml flask, provided with a hollow glass stopper, through which passes the tip of a 10 ml buret and a capillary tube, which connects the flask and the top of the buret. The upper end of the buret is closed with a glass stopper. A three-way stopcock establishes connection between the top of the buret and horizontal glass tubing of suitable length and internal diameter (5, 2 and 1 mm for titrations of solutions respectively 0.1, 0.01 and $0.001N$), the free extremity of which is bend downward and dips into water. A scale graduated in mm or 0.5 mm can be adjusted to any point of this tube. If solutions up to $0.05N$ are being titrated, the titration vessel should be protected from temperature changes by shielding it with asbestos paper. A magnetic stirrer provides the indispensable stirring of the sample solution.

GENERAL PROCEDURE

Transfer a measured volume of the sample solution to the titration flask and add other reagents and indicator if required. Connect the flask with the buret. Fill the horizontal glass tube with water, applying suction through the free extremity of the three-way stopcock. Turn the plug of this stopcock so as to establish connection only between the buret and the glass tube. Put the magnetic stirrer in motion.

Apply the O division of the scale to the extremity of the water column. Add measured increments of titrant (for instance 1 ml) to the sample solution, wait until the extremity of the water column in the tube remains steady, and then read in mm the length of the displaced water column. Plot the volume of titrant added against the length of the displaced water column. Extend the straight-line portions of the curve to intersect. The intersection marks the end-point.

It happens sometimes, chiefly during titration of dilute solutions, that the extremity of the water column in the tube does not remain sufficiently steady to allow an unequivocal reading. In such a case it is better to make the addition of the titrant and the reading of the water level in the tube at fixed intervals of time (1 or 2 minutes for example). If the concentration of the solutions is $0.01N$ or less, titrating and titrated solutions must be at the same temperature.

Titration of silver with hydrazine sulfate

Brown and Boyd[2] published recently a paper on an argentometric procedure for borohydride determination. The analysis is based on the reaction:

$$8\ Ag^+ + BH_4^- + 8\ OH^- \xrightarrow[\text{diamine}]{\text{ethylene}} 8\ Ag^\circ + H_2BO_3^- + 5\ H_2O \qquad (1)$$

The precipitated silver is removed by filtration and the excess silver ion in the solution is determined after acidification by the standard Volhard procedure. The authors state that "the analytical procedure could be considerably simplified if the excess silver ion could be titrated in presence of the precipitated silver. However, the black colour of the precipitated silver makes a colorimetric determination of the end-point impractical. Thus an attempt to apply the titration method of Bloom and McNabb[3] failed for this reason. No attempt was made to apply conductometric or potentiometric methods to such a titration".

The problem of titrating silver ion in presence of precipitated silver in alkaline medium, as posed by Brown and Boyd, can be solved by a gasometric titration procedure. The analysis involves direct titration of the mixture with standard hydrazine sulfate solution according to the equation:

$$4\ Ag^+ + N_2H_4 + 4\ OH^- \rightarrow 4\ Ag^\circ + N_2 + 4\ H_2O \qquad (2)$$

in the simple instrument described above. The same method can be used also for the direct titration of silver in an insoluble halide residue and for the indirect determination of cyanide or iodide ions. The graphs are of the type shown in Fig. 2. The intersection of the lines corresponding to the reaction (gas evolution) and to excess titrant (no gas evolution) signals the end-point.

Reagents

Hydrazine sulfate, 0.05, 0.025 and $0.0025M$ solutions.
Sodium hydroxide, 0.5 and $5N$ solutions.
Ammonium hydroxide, concentrated solution.

Procedure 1

Transfer 5.00 to 10.00 ml of the neutral sample solution which contains silver ions to the titration flask (or suspend a known amount of the insoluble silver salt in 5 ml of water), add sodium

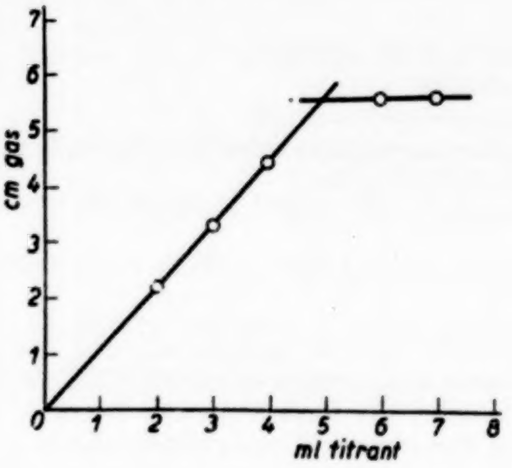

Fig. 2. Gasometric titration of 5.00 ml 0.0100M $AgNO_3$ solution with 0.0025M $N_2H_4.H_2SO_4$ solution (internal diameter of gas measuring tube 3 mm). End-point 4.98 ml (theoretical 5.00 ml).

hydroxide and concentrated ammonium hydroxide solutions (see Table I for quantities of reagents), connect the flask with the buret which contains the hydrazine sulfate solution and titrate following the instructions outlined above.

Interferences

Noble metals, copper(II) and mercury(II) ions, as well as oxidizing anions, such as iodate, permanganate and hypochlorite must be absent, since they also oxidize hydrazine in alkaline medium. Cyanide and iodide subtract their equivalent of silver ions from reduction, if the sodium hydroxide alkalinity is small. If sufficient NaOH is present neither those nor other anions which form even more soluble silver salts interfere with the analysis.

The ammonium hydroxide excess over the quantity necessary to dissolve the silver oxide should be as small as possible. A great excess of free ammonium hydroxide in the titration flask gives rise to contractions of the volume of the system when fresh volumes of titrating solution are introduced.

Titration of iodide with silver nitrate

According to the gasometric titration procedure outlined below iodide ions can be titrated directly with silver nitrate solution in alkaline medium. Hydrazine functions as gasometric indicator, reacting with excess silver ion after all the iodide has been transformed into silver iodide. The method is based on the fact that the very slightly soluble silver iodide does not react with hydrazine in moderately strong alkaline medium, whereas the cation of more soluble silver salts reacts according to equation 2.

The graphs are of the type shown in Fig. 3. The intersection of the line (abscissa) corresponding to the main reaction (no gas evolution) and the line corresponding to the reaction of the titrant with the indicator (gas evolution) marks the end-point.

Reagents

Silver nitrate, 0.2, 0.05 and 0.01M solutions.

Sodium hydroxide, 0.5N solution.

Ammonium hydroxide, concentrated solution.

Indicator: concentrated hydrazine sulfate solution, neutralized with 0.5N sodium hydroxide solution to the rose tint of phenolphthalein.

Procedure 2

Transfer 5.00 to 10.00 ml of the neutral sample solution, which contains iodide ion, to the titration flask, add concentrated ammonium hydroxide and indicator solutions (see Table II for quantities of reagents), connect the flask with the buret which contains the silver nitrate solution and titrate, following the instructions outlined above.

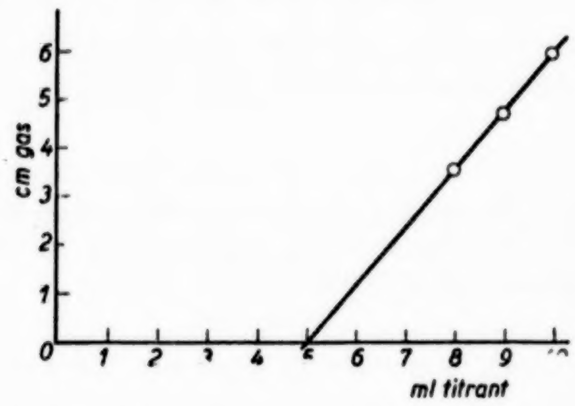

Fig. 3. Gasometric titration of 5.00 ml 0.01M KI solution with 0.01M $AgNO_3$ solution (internal diameter of gas measuring tube 3 mm). End-point 5.08 ml (indicator sodium fluoresceinate 5.12 ml).

Interferences

The sodium hydroxide concentration of the solution to be analysed is rather critical and its optimum depends on the halide content. Pure iodide solutions are best titrated in ammoniacal medium in absence or in presence of only small quantities of sodium hydroxide. Whereas 1 ml of 0.5N NaOH per 5 ml 0.2N iodide solution and 0.5 ml concentrated ammonium hydroxide solution gives good results, the same volume of 5N NaOH reduces the apparent iodide content of the sample to zero. The higher the halide content of the solution, the higher may be the NaOH concentration without leading to destruction of silver iodide. It is advantageous to work at the highest possible NaOH concentration, since it influences favorably the reaction velocity. At equimolecular concentrations the stability of the silver salt in ammoniacal medium against hydrazine at a given concentration of sodium hydroxide diminishes in the following order: CN^-, I^-, Br^-, Cl^-. It seems possible to use this property for the direct individual determination of these ions in their mixtures. For instance, Table II shows that at a slight NaOH alkalinity iodide can be determined in presence of chloride. Anions which form even more soluble silver salts do not interfere.

If the sample contains ions which react with hydrazine in alkaline medium, it must be treated with this substance prior to the titration until, upon further addition of hydrazine, no more gas evolution can be noted. Only those ions interfere which under such conditions are reduced to iodide.

SOME PAPERS TO APPEAR IN FIRST ISSUES

D. V. Andreani and C. H. Gray (London), Serum polysaccharides in diabetes mellitus.

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CLINICA CHIMICA ACTA

International Journal of Clinical Chemistry

When visiting hospital laboratories in foreign countries, one is impressed by the remarkable variation in techniques, choice of methods, indication for certain determinations and evaluation of results.

However, because clinical chemistry is a world-wide affair, the results and figures are distributed to many countries, despite the fact that they are not strictly comparable. Thus from the technical point of view alone, there is justification for establishing a strong international contact between the clinical chemists of every country in the world.

But there are more reasons. Few investigators have been adequately aware of the revolutionary development of chemical methods in clinical work and their increasing importance in diagnosis and therapy. The problems facing clinical chemists are essentially the same in every country and international contact is, under these conditions, of great importance.

A step in that direction is the foundation of this international journal on clinical chemistry. It will attempt to play its part in the work of synthetizing the efforts and achievements of clinical chemists throughout the world. We hope it will be of real service in establishing contact and developing mutual understanding between workers in this field, in bringing about standardization of methods, furthering the exchange of ideas, and promoting research, so that the journal will be of benefit to everyone in charge of a hospital laboratory or clinical chemical institution, to the profession and to mankind seeking for its health.

ELSEVIER

Titration of cyanide with silver nitrate

Cyanide is usually determined by the complex-formation method of Liebig-Denigès[4], according to which the ammoniacal sample solution, containing potassium iodide as indicator, is titrated with silver nitrate to the first permanent turbidity due to slightly soluble silver iodide.

The gasometric titration method for cyanide differs from the Liebig-Denigès method with respect to the indicator: hydrazine is used instead of iodide. It is based on the fact that the silver of the complex anion $[Ag(CN)_2]^-$ does not react with hydrazine in ammoniacal solution, whereas the cation of silver argentocyanide $Ag[Ag(CN)_2]$ reacts according to reaction 2.

The graphs are of the type shown in Fig. 3. The intersection of the line (abscissa) corresponding to the main reaction (no gas evolution) and the line corresponding to the reaction of the titrant with the indicator (gas evolution) marks the end-point.

Reagents

See *Titration of iodide.*

Procedure 3

Transfer 5.00 to 10.00 ml of the sample solution, which contains cyanide ion, to the titration flask, add concentrated ammonium hydroxide, sodium hydroxide and indicator solutions (see Table III for quantities of reagents). Connect the flask with the buret which contains the silver nitrate solution and titrate following the instructions outlined above.

Interferences

See *Titration of iodide.*

TABLE I

TITRATION OF SILVER NITRATE SOLUTION WITH HYDRAZINE SULFATE SOLUTION

$AgNO_3$ taken		*Additions to the $AgNO_3$ solution*	*$N_2H_4.H_2SO_4$ consumed*			Δ %
M	*ml*		*M*	*gasometric titration ml*	*theoretical ml*	
0.2000	5.00	0.5 ml conc. NH_4OH	0.0500	5.02		
0.2000	5.00	*idem*	0.0500	4.99		
0.2000	5.00	*idem* + 1 ml 0.5*N* NaOH	0.0500	4.98		
				mean 4.99	5.00	−0.20
0.1000	5.00	0.5 ml conc. NH_4OH + 1 ml 0.5*N* NaOH	0.0250	5.02		
0.1000	5.00	*idem*	0.0250	5.03		
0.1000	5.00	*idem*	0.0250	4.99		
				mean 5.01	5.00	+0.20
0.0100	5.00	0.1 ml conc. NH_4OH + 1 ml 0.5*N* NaOH	0.0025	5.06		
0.0100	5.00	*idem*	0.0025	4.98		
0.0100	5.00	*idem*	0.0025	5.05		
				mean 5.03	5.00	+0.60

TABLE II

TITRATION OF POTASSIUM IODIDE SOLUTION WITH SILVER NITRATE SOLUTION

KI taken		*Additions to the KI solution*	*AgNO$_3$ consumed*			Δ %
M	*ml*		*M*	*gasometric titration ml*	*with indicator sodium fluoresceinate*[4] *ml*	
0.01	5.00	0.5 ml conc. NH$_4$OH + 0.2 ml indicator	0.01	5.16		
0.01	5.00	*idem*	0.01	5.12		
0.01	5.00	*idem*	0.01	5.10		
				mean 5.13	mean 5.12	+0.19
0.05	5.00	0.5 ml conc. NH$_4$OH + 0.7 ml indicator	0.05	5.12		
0.05	5.00	*idem*	0.05	5.08		
				mean 5.10	mean 5.12	−0.39
0.2	5.00	0.5 ml conc. NH$_4$OH + 2.5 ml indicator } = A	0.2	5.00		
0.2	5.00	A	0.2	4.99		
0.2	5.00	A	0.2	4.98		
0.2	5.00	A + 1 ml 0.5N NaOH	0.2	5.00		
0.2	5.00	*idem*	0.2	5.00		
				mean 4.99	mean 5.00	−0.20
0.2	5.00	0.058 g NaCl A + 1 ml 0.5N NaOH	0.2	5.06		+1.20
0.2	5.00	0.116 g NaCl A + 1 ml 0.5N NaOH	0.2	5.03		+0.60
0.2	5.00	0.290 g NaCl A + 1 ml 0.5N NaOH	0.2	5.05		+1.00
0.2	5.00	0.580 g NaCl A + 1 ml 0.5N NaOH	0.2	5.05		+1.00
0.2	5.00	1.160 g NaCl A + 2 ml 0.5N NaOH	0.2	5.00		0.00

TABLE III

TITRATION OF POTASSIUM CYANIDE SOLUTION WITH SILVER NITRATE SOLUTION

KCN taken		*Additions to the KCN solution*	*AgNO$_3$ consumed*			Δ %
M	*ml*		*M*	*gasometric titration ml*	*Liebig-Denigès method*[4] *ml*	
0.1	5.00	0.5 ml conc. NH$_4$OH + 3 ml 0.5N NaOH + 1 ml indicator	0.05	4.85		
0.1	5.00	*idem*	0.05	4.80		
0.1	5.00	*idem*	0.05	4.84		
				mean 4.83	mean 4.82	+0.21

ACKNOWLEDGEMENTS

The author is indebted to Dr. TAYGOARA FLEURY DE AMORIM, Director of the Instituto de Química Agrícola, for the opportunity of carrying out the present work at this institution, and to the Conselho Nacional de Pesquisas for financial support.

SUMMARY

Several argentometric determinations have been worked out to show that the gasometric titration method is applicable not only to acid-base and redox reactions, but also to precipitation and complex-formation reactions. The processes reported allow the direct and indirect determination of iodide and cyanide, as well as the direct titration of silver ion in soluble and slightly soluble silver salts.

RÉSUMÉ

Plusieurs dosages argentométriques ont été élaborés démontrant que la méthode de titration gazométrique n'est pas seulement applicable aux réactions alcali-acidimétriques et aux réactions d'oxydo-réduction, mais qu'elle s'applique également aux réactions par précipitation et par formation de complexes. Les procédés décrits permettent le dosage direct et le dosage indirect des iodures et des cyanures, de même que le titrage direct de l'ion argent dans ses sels solubles ou peu solubles.

ZUSAMMENFASSUNG

Es wurden verschiedene argentometrische Bestimmungen ausgearbeitet, welche zeigen, dass die gasometrische Titrationsmethode nicht nur für Säure-Basen-Reaktionen und für Oxydo-Reduktions-Reaktionen anwendbar ist, sondern auch für Fällungs- und komplexbildende Reaktionen. Die beschriebenen Verfahren erlauben die direkte und die indirekte Bestimmung der Jodide und Cyanide, sowie auch die direkte Titration des Silberions in seinen löslichen oder wenig löslichen Salzen.

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MODIFIED ETHYLENEDIAMINETETRAACETATE METHOD FOR THE DIRECT ESTIMATION OF MAGNESIUM

by

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The use of ethylenediaminetetraacetic acid for the titration of calcium and magnesium is now well established[1]. The end-point is not very sharp however and various attempts have been made to improve it[2,3]. The present authors have adopted WILEY's method[4] for the determination of calcium. The latter is precipitated as molybdate and the magnesium is titrated with EDTA in the filtrate. The sum of the calcium and magnesium can be found first by direct titration. The method is suitable for the routine analysis of dolomite and limestone. Details of the analysis will be published later.

PROCEDURE

A slightly acid solution of a mixture of calcium and magnesium is first diluted to 50 ml and heated to about 80° C and then 5 to 10 ml of 10% ammonium molybdate solution are added and the solution is well stirred for a few minutes. Then 2 ml of NH_4OH-NH_4Cl buffer (pH 10) are added and the solution is boiled for a few minutes. Calcium molybdate precipitates out and the precipitation is complete in the alkaline pH. The solution is allowed to cool and then filtered through a Whatman No. 40 filter paper. The precipitate is washed several times with 10 ml portions of 1:3 alcohol water. The filtrate is then titrated with standard EDTA solution after the addition of 2 ml of NH_4OH-NH_4Cl buffer (pH 10) and 4-6 drops of 0.5% Solochrome Black T indicator solution. The presence of ammonium molybdate does not interfere with the EDTA titration using Solochrome Black T indicator.

SUMMARY

Magnesium and calcium are determined together, using EDTA solution with Solochrome Black T indicator. Calcium is then precipitated out as molybdate and the magnesium is determined in the filtrate.

RÉSUMÉ

Le magnésium et le calcium peuvent être dosés ensemble au moyen d'une solution d'EDTA, en utilisant le noir de solochrome T comme indicateur. Le calcium est alors précipité comme molybdate et le magnésium est ensuite dosé dans le filtrat.

ZUSAMMENFASSUNG

Magnesium und Calcium können zusammen mit EDTA-Lösung und unter Verwendung von Solochrom T Schwarz als Indikator bestimmt werden. Das Calcium wird dann als Molybdat gefällt und das Magnesium im Filtrat bestimmt.

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VOLUMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS

VIII. OXIDATION WITH CERIC SULPHATE FERROUS ETHYLENEDIAMINE SULPHATE METHOD

by

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The salts of quadrivalent cerium are the most versatile of the strong oxidizing agents, which may be used as standard solutions. Caraway and Oesper[1] showed that ferrous ethylenediamine sulphate, $FeSO_4.(CH_2{\cdot}NH_3)_2SO_4.4H_2O$, reacted stoichiometrically with ceric sulphate which is commonly employed in oxidimetric titrations.

In acid medium ceric sulphate reacts with ferrous ammonium sulphate, cuprous chloride, potassium thiocyanate, sodium thiosulphate, sodium nitrite, hydrogen peroxide, sodium oxalate, hydroquinone and pyruvic acid in accordance with the equations:

$$\begin{aligned}
Ce^{+4} + Fe^{+2} &\rightarrow Ce^{+3} + Fe^{+3}\\
2Ce^{+4} + Cu_2^{+2} &\rightarrow 2Ce^{+3} + 2Cu^{+2}\\
6Ce^{+4} + CNS^- + 4\,H_2O &\rightarrow 6Ce^{+3} + CN^- + SO_4^{-2} + 8H^+\\
2Ce^{+4} + 2S_2O_3^{-2} &\rightarrow 2Ce^{+3} + S_4O_6^{-2}\\
2Ce^{+4} + NO_2^- + H_2O &\rightarrow 2Ce^{+3} + NO_3^- + 2H^+\\
2Ce^{+4} + O_2^{-2} &\rightarrow 2Ce^{+3} + O_2\\
2Ce^{+4} + C_2O_4^{-2} &\rightarrow 2Ce^{+3} + 2CO_2\\
2Ce^{+4} + C_6H_4(OH)_2 &\rightarrow 2Ce^{+3} + C_6H_4O_2 + 2H^+\\
2Ce^{+4} + CH_3COCOOH + H_2O &\rightarrow 2Ce^{+3} + CH_3COOH + CO_2 + 2H^+
\end{aligned}$$

In the present investigation the substances have been determined indirectly by a volumetric method using ceric sulphate as oxidizing agent. The excess of standard ceric sulphate added to each of the substances was titrated with standard ferrous ethylenediamine sulphate solution using ferroin as an indicator.

EXPERIMENTAL

A known weight of each substance was mixed with an excess of standard ceric sulphate solution and the mixture acidified with sulphuric acid to keep its normality between 1 and 2*N*. In case of potassium thiocyanate the normality of the mixture with respect to sulphuric acid was kept between 4 and 6*N*. The mixtures containing sodium nitrite, sodium oxalate, hydroquinone and pyruvic acid were warmed to about 60° C, and the mixtures containing cuprous chloride and potassium thiocyanate were heated for about ten minutes and then allowed to cool. In each case the excess of ceric sulphate was titrated against standard ferrous ethylenediamine sulphate solution using ferroin as an indicator.

Ceric sulphate was standardized with ferrous ethylenediamine sulphate (FES) which was prepared by the method of Caraway and Oesper *(loc. cit.)*.

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The results given in Tables I to IX show that the substances can be determined indirectly by the volumetric method, using ceric sulphate as an oxidizing agent in acid medium.

TABLE I

FERROUS AMMONIUM SULPHATE

$FeSO_4.(NH_4)_2SO_4.6H_2O$ taken (g)	*N/20 $Ce(SO_4)_2$ added (ml)*	*N/20 FES used for excess $Ce(SO_4)_2$ (ml)*	*N/20 $Ce(SO_4)_2$ used by $FeSO_4.(NH_4)_2SO_4.6H_2O$ (ml)*	*$FeSO_4.(NH_4)_2SO_4.6H_2O$ found (g)*
0.0980	10.00	5.00	5.00	0.0981
0.1980	20.00	9.90	10.10	0.1981
0.2950	25.00	9.95	15.05	0.2951
0.3932	30.00	9.95	20.05	0.3932
0.4902	40.00	15.00	25.00	0.4903

TABLE II

CUPROUS CHLORIDE

Cu_2Cl_2 taken (g)	*N/20 $Ce(SO_4)_2$ added (ml)*	*N/20 FES used for excess $Ce(SO_4)_2$ (ml)*	*N/20 $Ce(SO_4)_2$ used by Cu_2Cl_2 (ml)*	*Cu_2Cl_2 found (g)*
0.0247	20.00	15.00	5.00	0.0248
0.0494	20.00	10.00	10.00	0.0495
0.0740	20.00	5.00	15.00	0.0742
0.0989	30.00	10.00	20.00	0.0990
0.1136	43.00	20.00	23.00	0.1138

TABLE III

POTASSIUM THIOCYANATE

KCNS taken (g)	*N/20 $Ce(SO_4)_2$ added (ml)*	*N/20 FES used for excess $Ce(SO_4)_2$ (ml)*	*N/20 $Ce(SO_4)_2$ used by KCNS (ml)*	*KCNS found (g)*
0.0040	10.00	5.00	5.00	0.0041
0.0080	20.00	9.90	10.10	0.0082
0.0121	30.00	15.00	15.00	0.0121
0.0160	35.00	15.00	20.00	0.0162
0.0201	40.00	15.00	25.00	0.0202

TABLE IV

SODIUM THIOSULPHATE

$Na_2S_2O_3.5H_2O$ taken (g)	*N/20 $Ce(SO_4)_2$ added (ml)*	*N/20 FES used for excess $Ce(SO_4)_2$ (ml)*	*N/20 $Ce(SO_4)_2$ used by $Na_2S_2O_3.5H_2O$ (ml)*	*$Na_2S_2O_3.5H_2O$ found (g)*
0.0632	10.00	4.90	5.10	0.0633
0.1245	20.00	9.95	10.05	0.1247
0.1740	25.00	10.95	14.05	0.1744
0.2478	35.00	15.00	20.00	0.2482
0.3098	37.00	12.00	25.00	0.3103

TABLE V

SODIUM NITRITE

$NaNO_2$ taken (g)	*N/20 $Ce(SO_4)_2$ added* (ml)	*N/20 FES used for excess $Ce(SO_4)_2$* (ml)	*N/20 $Ce(SO_4)_2$ used by $NaNO_2$* (ml)	*$NaNO_2$ found* (g)
0.0140	15.00	6.80	8.20	0.0141
0.0204	20.00	8.10	11.90	0.0205
0.0258	25.00	10.00	15.00	0.0259
0.0327	35.00	16.00	19.00	0.0328
0.0396	40.00	17.00	23.00	0.0397

TABLE VI

HYDROGEN PEROXIDE

H_2O_2 taken (g)	*N/20 $Ce(SO_4)_2$ added* (ml)	*N/20 FES used for excess $Ce(SO_4)_2$* (ml)	*N/20 $Ce(SO_4)_2$ used by H_2O_2* (ml)	*H_2O_2 found* (g)
0.0035	15.00	11.00	4.00	0.0034
0.0102	20.00	7.90	12.10	0.0103
0.0137	30.00	13.70	16.30	0.0138
0.0171	35.00	14.60	20.40	0.0173
0.0213	45.00	19.80	25.20	0.0214

TABLE VII

SODIUM OXALATE

$(COONa)_2$ taken (g)	*N/20 $Ce(SO_4)_2$ added* (ml)	*N/20 FES used for excess $Ce(SO_4)_2$* (ml)	*N/20 $Ce(SO_4)_2$ used by $(COONa)_2$* (ml)	*$(COONa)_2$ found* (g)
0.0240	15.00	7.80	7.20	0.0241
0.0334	20.00	10.00	10.00	0.0335
0.0498	30.00	15.10	14.90	0.0499
0.0670	35.00	15.00	20.00	0.0670
0.0835	45.00	20.05	24.95	0.0836

TABLE VIII

HYDROQUINONE

$C_6H_4(OH)_2$ taken (g)	*N/20 $Ce(SO_4)_2$ added* (ml)	*N/20 FES used for excess $Ce(SO_4)_2$* (ml)	*N/20 $Ce(SO_4)_2$ used by $C_6H_4(OH)_2$* (ml)	*$C_6H_4(OH)_2$ found* (g)
0.0138	10.00	4.95	5.05	0.0139
0.0275	20.00	9.95	10.05	0.0276
0.0412	25.00	10.00	15.00	0.0413
0.0548	30.00	10.00	20.00	0.0550
0.0686	40.00	15.00	25.00	0.0688

TABLE IX

PYRUVIC ACID

$CH_3COCOOH$ taken (g)	N/20 $Ce(SO_4)_2$ added (ml)	N/20 FES used for excess $Ce(SO_4)_2$ (ml)	N/20 $Ce(SO_4)_2$ used by $CH_3COCOOH$ (ml)	$CH_3COCOOH$ found (g)
0.0109	10.00	5.00	5.00	0.0110
0.0218	20.00	10.00	10.00	0.0220
0.0327	30.00	15.05	14.95	0.0329
0.0440	35.00	15.00	20.00	0.0440
0.0528	45.00	21.00	24.00	0.0528

SUMMARY

Ceric sulphate has been used as an oxidizing agent in acid medium for the indirect volumetric determinations of ferrous ammonium sulphate, cuprous chloride, potassium thiocyanate, sodium thiosulphate, sodium nitrite, hydrogen peroxide, sodium oxalate, hydroquinone and pyruvic acid. The excess of ceric sulphate added to each of the substances in acid medium was titrated with standard ferrous ethylenediamine sulphate solution using ferroin as an indicator.

RÉSUMÉ

Le sulfate de cérium(IV) peut être utilisé comme oxydant, en milieu acide, pour le dosage volumétrique indirect du sulfate de fer(II) et d'ammonium, du chlorure de cuivre(I), du thiocyanate de potassium, du thiosulfate de sodium, du nitrite de sodium, du peroxyde d'hydrogène, de l'oxalate de sodium, de l'hydroquinone et de l'acide pyruvique. L'excès de sulfate de cérium(IV) ajouté à chacune de ces substances, en milieu acide, est titré avec une solution de sulfate de fer(II) et d'éthylènediamine, en présence de ferroïne comme indicateur.

ZUSAMMENFASSUNG

Cer(IV)sulfat wurde in saurem Medium als Oxydationsmittel für die indirekten volumetrischen Bestimmungen von Ammoniumferrosulfat, Kupfer(I)chlorid, Kaliumthiocyanat, Natriumthiosulfat, Natriumnitrit, Wasserstoffperoxyd, Natriumoxalat, Hydrochinon und Brenztraubensäure verwendet. Der Überschuss an Cer(IV)sulfat, der jeder der oben aufgeführten Substanzen in saurem Medium zugesetzt wurde, lässt sich mit eingestellter Eisen(II)äthylendiaminsulfatlösung zurücktitrieren. Ferroin dient dabei als Indikator.

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DETERMINATION OF THIOUREA AND TETRAMETHYLTHIOUREA AN IODINE-ARSENITE METHOD

by

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CUTHILL AND ATKINS[1] studied the oxidation of thiourea by alkaline iodine and adopted this reaction for the quantitative determination of thiourea:

$$CS(NH_2)_2 + 10\ NaOH + 4\ I_2 \rightarrow CO(NH_2)_2 + Na_2SO_4 + 8\ NaI + 5\ H_2O.$$

An aqueous solution of thiourea was mixed with an equal volume of $2N$ sodium hydroxide to which a measured excess of standard iodine solution was added. After 15 minutes the system was acidified with $4N$ sulphuric acid and the unreacted iodine titrated with standard thiosulphate. However, the accuracy of results obtained by their procedure depended on various factors such as the order of mixing, duration of standing and the concentration of iodine and alkali. These observations emphasized the necessity for a reinvestigation of the CUTHILL-ATKINS method. The present work presents a modified procedure for determining thiourea depending on the titration of excess iodine with standard As_2O_3 in the appropriate pH range. Conditions and results are also recorded for the determination of tetramethylthiourea.

EXPERIMENTAL

A stock solution of thiourea was prepared by dissolving an accurately weighed quantity of E. Merck's guaranteed reagent in water. Tetramethylthiourea was prepared starting from tetramethylthiuram disulphide[2]. The purified product melted at 78° C and its aqueous solution was obtained by dissolving an exactly weighed quantity in water.

To an aliquot of the thiourea solution in a glass-stoppered Erlenmeyer flask were added sufficient sodium hydroxide to maintain an overall normality of 1 to $3N$ and a measured excess of iodine solution. The contents of the flask were swirled and set aside in ice-cold water for about 30 minutes. The alkali was just neutralized with $2N$ HCl or H_2SO_4 and the pH of the system raised by introducing an excess of borax-boric acid buffer. The buffer solution was prepared by dissolving 8 g and 4 g of crystallized borax and pure boric acid respectively in 100 ml of water[3]. The unreacted iodine was then titrated with $0.1N$ arsenious oxide solution to the usual starch end-point[4]. The difference in the initial and final titre values of As_2O_3 corresponds to the quantity of iodine consumed and hence to the amount of thiourea present in the system in accordance with the following equations:

$$8\ NaOH + 4\ I_2 \rightarrow 4\ NaIO + 4\ NaI + 4\ H_2O \quad \ldots\ldots \quad (1)$$

$$CS(NH_2)_2 + 4\ NaIO + H_2O \rightarrow CO(NH_2)_2 + 4\ NaI + H_2SO_4 \quad \ldots\ldots \quad (2)$$

$$2\ As_2O_3 + 4\ I_2 + 4\ H_2O \rightarrow 2\ As_2O_5 + 8\ HI \quad \ldots\ldots \quad (3)$$

Thus $1\ CS(NH_2)_2 = 4\ I_2 = 2\ As_2O_3$, or in other words, 1 ml of $1N$ As_2O_3 corresponds to 0.009500 g of thiourea. A representative set of results is given in Table I. It includes also the values obtained by thiosulphate titrations.

References p. 513.

TABLE I

Overall normality of NaOH = 1·3*N*

Expt. No.	*Vol. of thiourea taken (ml)*	*Vol. of iodine added (ml)*	*Vol. of 0.1N $Na_2S_2O_3$ (ml)*			*Vol. of 0.1N As_2O_3 (ml)*			*$(NH_2)_2CS$ (g)*			*Error %*	
			= I_2 added	*= I_2 unreacted*	*= I_2 reacted*	*= I_2 added*	*= I_2 unreacted*	*= I_2 reacted*	*By weight (x)*	*By thio (a)*	*By As_2O_3 (b)*	*(a)*	*(b)*
1	10.0	20.0	20.20	16.00	4.20	20.20	16.00	4.20	0.00399	0.003989	0.003989	0.025	0.025
2	20.0	25.0	25.25	16.85	8.40	25.25	16.85	8.40	0.00798	0.007978	0.007978	0.025	0.025
3	10.0	30.0	30.30	13.55	16.75	30.30	13.55	16.75	0.01596	0.01592	0.01592	0.25	0.25
4	20.0	60.0	60.60	27.20	33.40	60.60	27.10	33.50	0.03192	0.03173	0.03182	0.66	0.33
5	25.0	70.0	70.70	28.95	41.75	70.70	28.80	41.90	0.03990	0.03966	0.03980	0.60	0.25
6	30.0	90.0	90.90	40.65	50.25	90.90	40.60	50.30	0.04788	0.04773	0.04778	0.31	0.20
7	40.0	100.0	101.0	34.00	67.00	101.0	33.90	67.10	0.06384	0.06365	0.06374	0.32	0.16

TABLE IV

Overall normality of NaOH = ∼ 0.4*N*

Expt. No.	*Vol. of $(NMe_2)_2CS$ taken (ml)*	*Vol. of iodine added (ml)*	*Vol. of 0.1N $Na_2S_2O_3$ (ml)*			*Vol. of 0.1N As_2O_3 (ml)*			*$(NMe_2)_2CS$ (g)*			*Error %*	
			= I_2 added	*= I_2 unreacted*	*= I_2 reacted*	*= I_2 added*	*= I_2 unreacted*	*= I_2 reacted*	*By weight (x)*	*By thio (a)*	*By As_2O_3 (b)*	*(a)*	*(b)*
1	20.0	10.0	10.10	5.10	5.00	10.10	5.15	4.95	0.008200	0.008250	0.008168	0.62	0.40
2	10.0	20.0	20.20	10.20	10.00	20.20	10.20	10.00	0.01640	0.01650	0.01650	0.62	0.62
3	20.0	30.0	30.30	10.40	19.90	30.30	10.40	19.90	0.03280	0.03284	0.03284	0.12	0.12
4	25.0	40.0	40.40	15.40	25.00	40.40	15.50	24.90	0.04100	0.04125	0.04109	0.61	0.22
5	30.0	40.0	40.40	10.55	29.85	40.40	10.55	29.85	0.04920	0.04925	0.04925	0.10	0.10
6	40.0	50.0	50.50	10.70	39.80	50.50	10.70	39.80	0.06560	0.06567	0.06567	0.10	0.10

Tetramethylthiourea was determined by adopting the above experimental procedure but maintaining the total sodium hydroxide concentration in the system between 0.1 and 0.6N. The reaction may be expressed as follows:

$$CS(NMe_2)_2 + 4\ NaIO + H_2O \rightarrow CO(NMe_2)_2 + 4\ NaI + H_2SO_4 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

It therefore follows that 1 $CS(NMe_2)_2 \equiv 4\ I_2 \equiv 2\ As_2O_3$, or, in other words 1 ml of 1N As_2O_3 is equal to 0.01650 g of tetramethylthiourea. Results for a typical series of experiments are given in Table IV which also includes the values obtained by the thiosulphate method.

TABLE II

EFFECT OF NaOH CONCENTRATION

Volume of thiourea = 10 ml. Iodine added = 30 ml. Reaction time = 30 minutes

Expt. No.	*Overall normality of NaOH (N)*	*Volume of 0.1N As_2O_3 (ml)*			*$(NH_2)_2CS$ (g)*		*Error %*
		≡ I_2 added	*≡ I_2 unreacted*	*≡ I_2 reacted*	*Weighed*	*Calcd.*	
1	0.4	30.30	13.70	16.60	0.01596	0.01577	−1.2
2	0.8	30.30	13.65	16.65	0.01596	0.01581	−0.93
3	1.0	30.30	13.55	16.75	0.01596	0.01592	−0.25
4	1.5	30.30	13.55	16.75	0.01596	0.01592	−0.25
5	2.0	30.30	13.55	16.75	0.01596	0.01592	−0.25
6	2.5	30.30	13.55	16.75	0.01596	0.01592	−0.25
7	3.0	30.30	13.55	16.75	0.01596	0.01592	−0.25

TABLE III

EFFECT OF IODINE CONCENTRATION

Volume of thiourea = 20 ml. Overall normality of NaOH = 1N. Reaction times = 30 minutes

Expt. No.	*Vol. of iodine added (ml)*	*Volume of 0.1N As_2O_3 (ml)*			*$(NH_2)_2CS$ (g)*		*Error %*
		≡ I_2 added	*≡ I_2 unreacted*	*≡ I_2 reacted*	*weighed*	*calcd.*	
1	40.0	40.40	7.30	33.10	0.03192	0.03145	−1.5
2	50.0	50.50	17.30	33.20	0.03192	0.03154	−1.2
3	60.0	60.60	27.10	33.50	0.03192	0.03182	−0.31
4	80.0	80.80	47.30	33.50	0.03192	0.03182	−0.31
5	100.0	101.0	67.50	33.50	0.03192	0.03182	−0.31

TABLE V

EFFECT OF NaOH CONCENTRATION

Volume of tetramethylthiourea = 10 ml. Iodine added = 20 ml. Reaction time = 30 minutes

Expt. No.	*Overall normality of NaOH (N)*	*Volume of 0.1N As_2O_3 (ml)*			*$(NMe_2)_2CS$ (g)*		*Error %*
		≡ I_2 added	*≡ I_2 unreacted*	*≡ I_2 reacted*	*weighed*	*calcd.*	
1	0.1	20.20	10.20	10.00	0.01640	0.01650	+0.62
2	0.2	20.20	10.20	10.00	0.01640	0.01650	+0.62
3	0.3	20.20	10.20	10.00	0.01640	0.01650	+0.62
4	0.4	20.20	10.20	10.00	0.01640	0.01650	+0.62
5	0.6	20.20	10.20	10.00	0.01640	0.01650	+0.62
6	0.9	20.20	10.10	10.10	0.01640	0.01666	+1.6
7	1.2	20.20	10.00	10.20	0.01640	0.01683	+2.6

TABLE VI

EFFECT OF IODINE CONCENTRATION

Volume of tetramethylthiourea = 10 ml. Overall normality of NaOH = 0.4*N*
Reaction time = 30 minutes

Expt. No.	*Vol. of iodine added (ml)*	*Volume of 0.1N As_2O_3 (ml)*			*$(NMe_2)_2CS$ (g)*		*% Error*
		≡ I_2 added	*≡ I_2 unreacted*	*≡ I_2 reacted*	*weighed*	*calcd.*	
1	15.0	15.15	5.25	9.90	0.01640	0.01633	−0.44
2	20.0	20.20	10.20	10.00	0.01640	0.01650	+0.62
3	30.0	30.30	20.30	10.00	0.01640	0.01650	+0.62
4	40.0	40.40	30.40	10.00	0.01640	0.01650	+0.62
5	50.0	50.50	40.50	10.00	0.01640	0.01650	+0.62

DISCUSSION

When iodine solution, followed by sodium hydroxide, was added to thiourea, low results were obtained owing to the formation of formamidine disulphide and/or the subsequent precipitation of sulphur. This inherent error was negligible when the addition of alkali preceeded that of iodine (*cf.* EXPERIMENTAL). Incidentally these observations confirm the earlier findings of CUTHILL AND ATKINS[1].

Experiments performed with varying quantities of sodium hydroxide revealed that the oxidation of thiourea by iodine was quantitative over a fairly wide range of alkali concentration (*cf.* Table II). However, normalities below 1*N* yielded results about 1% low. Although less than twice the theoretical amount of iodine was insufficient for quantitative oxidation of thiourea, a large excess was found to have little adverse effect on the accuracy of the results (*cf.* Table III). Furthermore, the reaction stoichiometry remained unaltered even when the duration of standing exceeded 30 minutes. Hence the optimum conditions for the accurate determination of thiourea are: (1) overall alkalinity of the system between 1 and 3*N*, (2) 2 to 3-fold excess iodine and a reaction time of about 30 minutes. The present method thus affords the determination of 0.004 to 0.064 g of thiourea in a single operation.

The tetramethylthiourea-iodine reaction proceeds according to equation (4) in an overall sodium hydroxide concentration between 0.1 and 0.6*N* (*cf.* Table V). Normalities above 0.6*N* invariably gave high results. The iodine concentration was not critical provided a sufficient excess was maintained (*cf.* Table VI). Under these initial operative conditions the method provides an excellent means of determining 0.008 to 0.06 g of tetramethylthiourea.

It is well known that the reversible reaction between iodine and arsenious oxide, $As_2O_3 + 2\,I_2 + 2\,H_2O \rightleftarrows As_2O_5 + 4\,HI$, proceeds in the forward direction when the hydriodic acid is removed as soon as it is formed. This is usually accomplished by buffers like NaH_2PO_4-Na_2HPO_4, $NaHCO_3$-CO_2 or borax-boric acid in the pH range 4-11[5,6]. Free alkalies, owing to their secondary reactions with iodine, are not recommended for this purpose. In the present work a mixture of borax and boric acid was preferred, since phosphate buffer was slow and inconvenient, and sodium bicarbonate generally caused a partial loss of iodine due to the evolution of carbon dioxide on acidification. It may be mentioned that the present method of determining thiourea and tetramethylthiourea is simpler than that of CUTHILL AND ATKINS, and offers an additional advantage of using a primary standard, As_2O_3.

Further work on the reactions involved in the oxidation of thiourea and its derivatives by iodine in weakly alkaline medium and their adaptibility to direct titration using chemical indicator and/or electrometric end-points is now in progress.

The author extends his grateful thanks to Professor S. S. JOSHI for research facilities.

SUMMARY

Oxidation of thiourea and tetramethylthiourea by alkaline iodine is studied. The reaction is found to proceed quantitatively over a wide range of experimental conditions. A method of estimating thiourea and its tetramethyl derivative is developed, based on the titration of the excess iodine against standard arsenious oxide in a suitable pH range.

RÉSUMÉ

Une étude a été effectuée sur l'oxydation de la thiourée et de la tétraméthylthiourée par l'iode, en solution alcaline. La réaction est quantitative dans des conditions expérimentales variées. Une méthode est proposée pour le dosage de la thiourée et de la tétraméthylthiourée; elle est basée sur le titrage de l'iode ajouté en excès, au moyen d'anhydride arsénieux, à un pH convenable.

ZUSAMMENFASSUNG

Es wurde eine Untersuchung ausgeführt über die Oxydation von Thioharnstoff und Tetramethylthioharnstoff mit Jod in alkalischer Lösung. Die Reaktion ist bei verschiedenen Versuchsbedingungen quantitativ. Es wird eine Methode für die Bestimmung von Thioharnstoff und Tetramethylthioharnstoff vorgeschlagen; sie basiert auf der Titration des im Überschuss zugefügten Jods mittels arseniger Säure bei einem geeigneten pH.

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A RAPID AND PRECISE METHOD FOR THE DETERMINATION OF OXYGEN IN CERTAIN GASES

MODIFIED BRADY METHOD

by

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INTRODUCTION

The extended use of experimental systems involving liquid metals occasions continued interest in the oxygen-content of the inactive gases which are to be used to blanket such systems.

Instruments which utilize physicochemical properties have been designed for determination of oxygen in gases. The Beckman oxygen analyser based on the theory of PAULING'S[1] Oxygen Meter depends on the paramagnetic nature of oxygen. A method described by PEPKOWITZ[2] converts the oxygen to water and measures the dew point. Such methods, while rapid in response, are not sensitive to minute quantities of oxygen such as one part per million or less.

A diversity of colorimetric methods for the determination of small amounts of oxygen in gas have been proposed. One of the most sensitive methods for small amounts of oxygen is that of WINKLER[3] in which oxygen is absorbed into neutral or alkaline manganous solution and then determined as iodine. WINSLOW AND LIEBHAFSKY[4] adapted this method to determine small quantities of oxygen in gases. PEPKOWITZ[5] adapted the method further, permitting the analysis of small quantities of gas (one liter or less) with a precision of at least one ppm oxygen. By using a modified vacuum technique and by using purer and more sensitive reagents SILVERMAN AND BRADSHAW[6] improved the precision of the method to ±0.33 part per million oxygen.

This colorimetric method is sensitive to small amounts of oxygen of one microliter or less and thus can be used to analyse small quantities of gas, such as one liter. Its disadvantage lies in the time (four hours) involved in completing one analysis. Several samples can be run concurrently but the maximum number of determinations which can be done by one operator is four per day.

BRADY[7] described a very satisfactory apparatus which requires larger volumes of sample gas to determine one part per million of oxygen. In this method oxygen is absorbed into an alkaline solution of sodium anthraquinone-beta-sulfonate, which changes the solution from red to colorless. The course of oxidation is followed by observing the decrease in absorbance using a green filter in a photoelectric colorimeter.

The BRADY method was modified as follows so as to be suitable for the determinations of still lower oxygen-concentrations and to obtain greater accuracy and precision:

Tygon joints were eliminated to prevent oxygen diffusion.

Flexibility was attained by the use of ball and socket joints held together firmly by spring clamps.

A more efficient gas-liquid pumping system was used, permitting greater sensitivity to small amounts of oxygen.

A Beckman model DU spectrophotometer was used in place of a Klett colorimeter.

The last two modifications extended the lower limit of detection to 0.005 part per million oxygen. The reported range of the BRADY[7] method was 1 to 100 parts per million. The precision of the method was improved by calculating the oxygen-concentration from the slope of the absorbance-change rather than from the difference in absorbance (BRADY's method) between two arbitrary points. The optical response of a Beckman-type spectrophotometer is necessary equipment for precision analysis.

The accuracy of the method was enhanced by using an improved method for the de-oxidation of the helium gas in order to obtain a very low oxygen-content carrier-gas for calibration.

APPARATUS

The modified apparatus used is shown schematically in Fig. 1. Ball and socket joints were placed at strategic points to promote flexibility and to permit ready disassembly of the system for cleaning and repair.

Previous experimental work in this laboratory has shown that oxygen can diffuse through

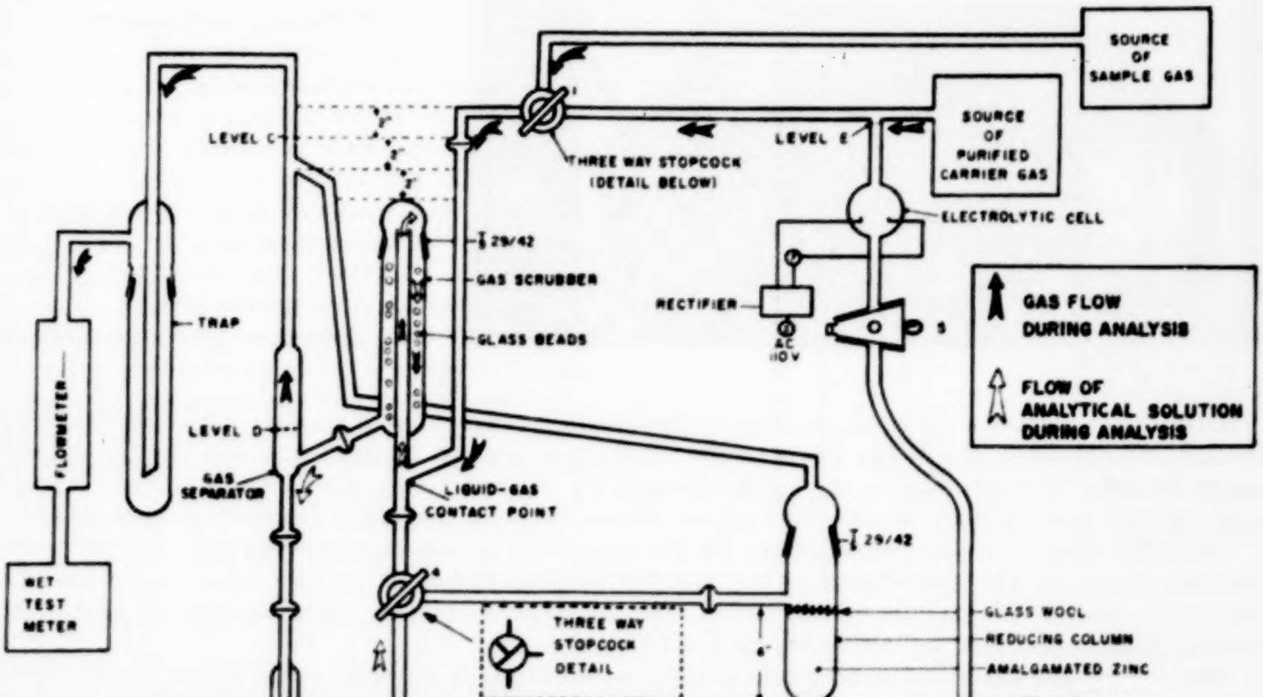
SOURCE OF SAMPLE GAS
SOURCE OF PURIFIED CARRIER GAS
LEVEL C
LEVEL E
THREE WAY STOPCOCK (DETAIL BELOW)
1
ELECTROLYTIC CELL
29/42
GAS SCRUBBER
GLASS BEADS
RECTIFIER
AC 110 V
5
GAS FLOW DURING ANALYSIS
FLOW OF ANALYTICAL SOLUTION DURING ANALYSIS
TRAP
FLOWMETER
LEVEL D
GAS SEPARATOR
LIQUID-GAS CONTACT POINT
WET TEST METER
4
THREE WAY STOPCOCK DETAIL
29/42
GLASS WOOL
REDUCING COLUMN
AMALGAMATED ZINC
GLASS WOOL
6"
ABSORPTION CELL
1¾"
3
2
RESERVOIR BOTTLE ANALYTICAL SOLUTION
A
B
SULFURIC ACID RESERVOIR BOTTLE

Fig. 1. Schematic of modified BRADY apparatus for oxygen analysis.

tygon tubing; for this reason tygon is not used in the system except as hose connections to the reservoir bottles. This is permissible since this part of the system is cut off from the stream of gas flow during the course of the analysis.

In preparation, the analytical solution is passed through a reducing column containing amalgamated zinc and then the solution is ready to be circulated through the analytical portion of the system.

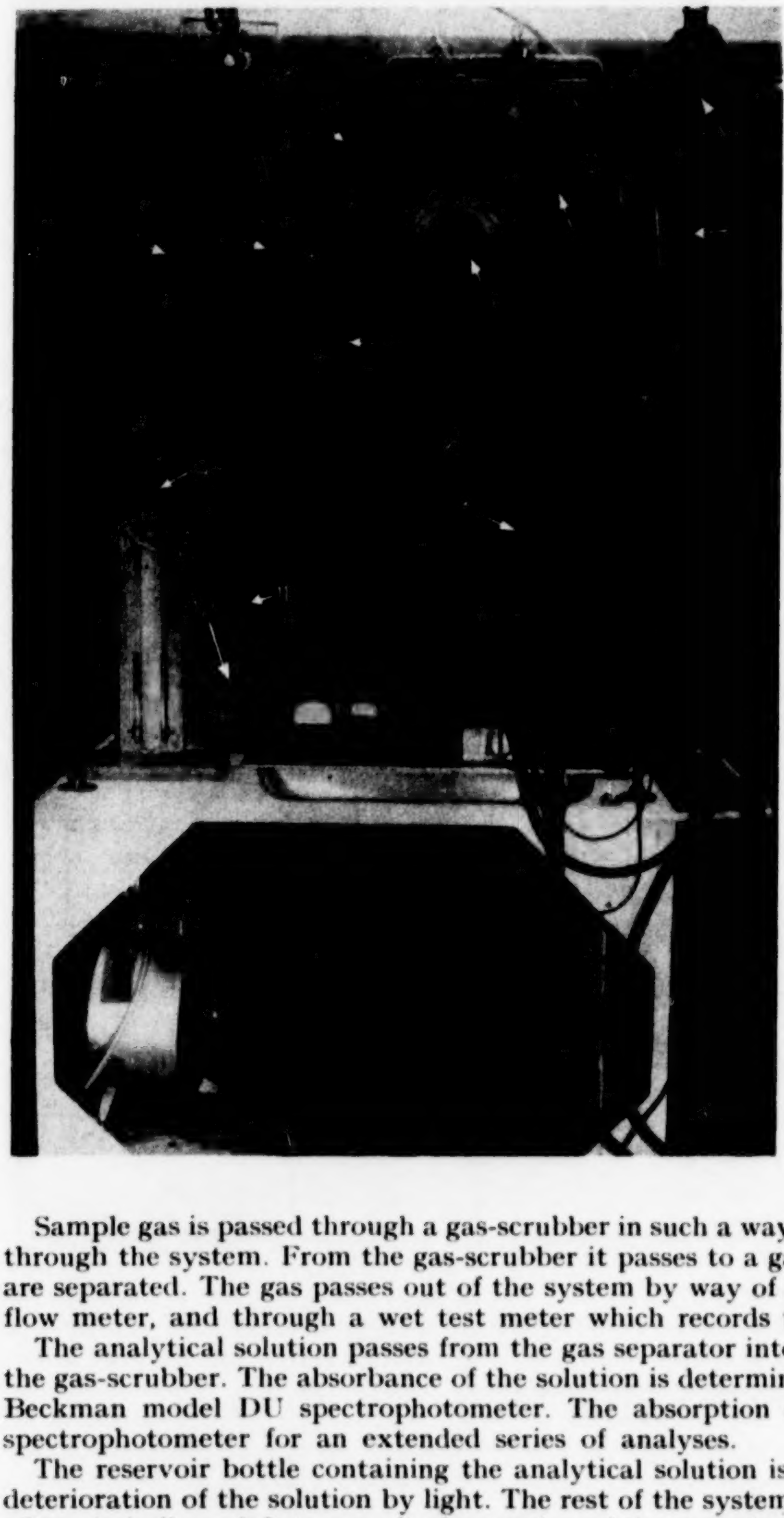

Fig. 1A.

1 Reservoir bottle (anal. solution)
2 Reservoir bottle (sulphuric acid)
3 Electrolytic cell
4 Milliammeter
5 Scrubber
6 Gas separator
7 Trap
8 Liquid gas contact point
9 Flow meter
10 Reducing column
11 Absorption cell
12 Beckman spectrophotometer

Sample gas is passed through a gas-scrubber in such a way that it pumps the analytical solution through the system. From the gas-scrubber it passes to a gas separator where the liquid and gas are separated. The gas passes out of the system by way of a trap for excess moisture, through a flow meter, and through a wet test meter which records the total amount of sample-gas.

The analytical solution passes from the gas separator into an absorption cell and back up into the gas-scrubber. The absorbance of the solution is determined at regular intervals by means of a Beckman model DU spectrophotometer. The absorption cell is mounted permanently in the spectrophotometer for an extended series of analyses.

The reservoir bottle containing the analytical solution is covered with black tape to prevent deterioration of the solution by light. The rest of the system is partially covered with black tape. "Peep-holes" are left to permit observation of the pumping action and the color of the solution. The area of the absorption cell immediately above the spectrophotometer unit is completely covered with black tape to prevent stray light interfering with absorbance readings.

The details of the gas-scrubber section are shown in Fig. 2A. The dimensions are critical in order to obtain maximum pumping efficiency. The sample gas enters through 8-mm glass tubing and is deflected by a piece of 4-mm glass tubing into the analyticalsloution. The gas forces some liquid up the 4-mm tubing, but the 4-mm and 8-mm tubing are sealed together strategically, as shown, to prevent liquid and gas passing up between them. From the top of this tubing the

References p. 526.

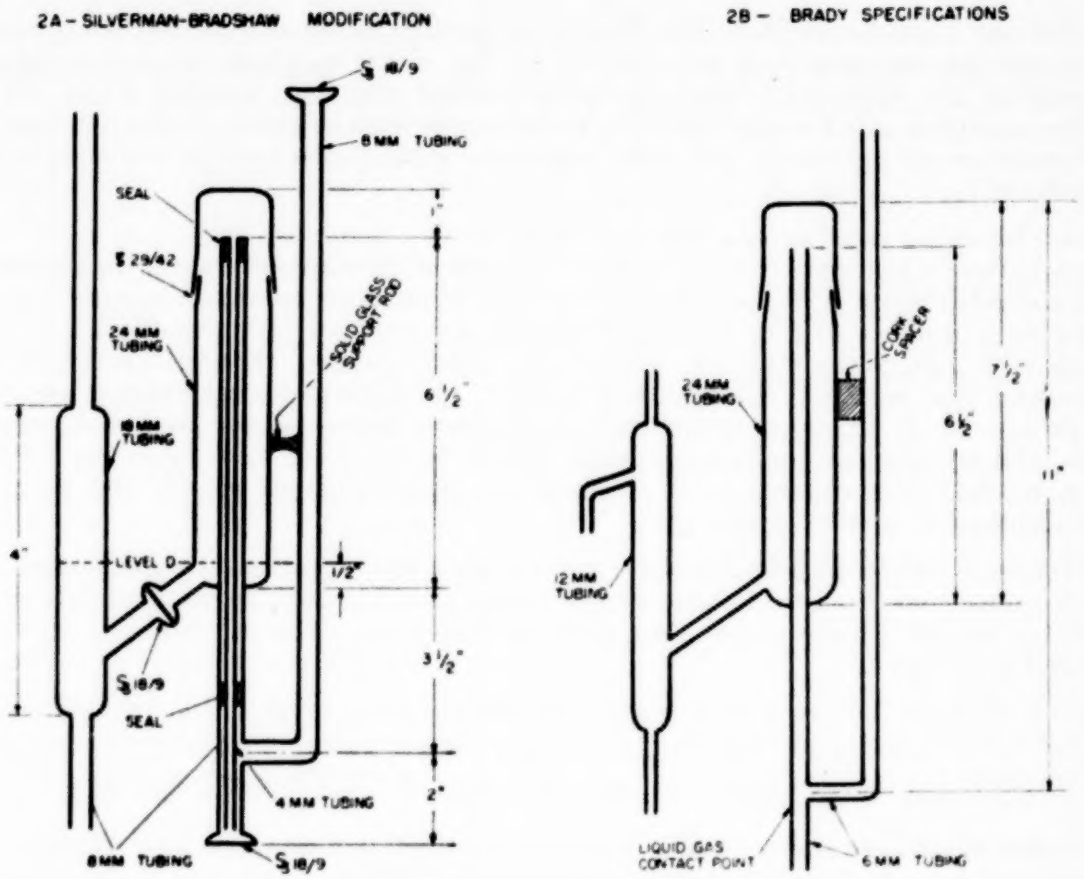
2A – SILVERMAN-BRADSHAW MODIFICATION
2B – BRADY SPECIFICATIONS
S 18/9
8 MM TUBING
SEAL
S 29/42
24 MM TUBING
18 MM TUBING
SOLID GLASS SUPPORT ROD
1"
6 1/2"
4"
LEVEL D
1/2"
3 1/2"
S 18/9
SEAL
4 MM TUBING
2"
8 MM TUBING
S 18/9
CORK SPACER
24 MM TUBING
7 1/2"
6 1/2"
11"
12 MM TUBING
LIQUID GAS CONTACT POINT
6 MM TUBING

Fig. 2. Details of gas-scrubber
2A-SILVERMAN-BRADSHAW modification
2B-Brady specifications

liquid splashes into a 24-mm section filled with glass beads in order to obtain maximum mixing action. Both gas and liquid pass into the 18-mm liquid-gas separator.

In order to calibrate the system, oxygen is generated in an electrolytic cell (Fig. 3). The cell consists of a 50-ml bulb with tungsten wire-leads inserted into the glass. The current source is a 110-volt 60-cycle supply put through a rectifying control unit which converts the alternating current input to low amperage (6 milliamperes) direct current. The current is read on a 0 to 25 milliammeter accurate to one percent.

In order to obtain a carrier-gas low in oxygen-content for calibration, NaK bubblers containing 700 to 5,000 ml of liquid NaK eutectic (78 percent potassium) were used. (A compact NaK bubbler to be used for laboratory experiments is currently in process of design.)

REAGENTS

Scrubbing solution, analytical reagent. Dissolve 0.033 g of sodium anthraquinone-beta-sulfonate in 300 ml of distilled water by heating gently. Cool the solution to room temperature. Add 10 ml of 30 percent sodium hydroxide solution by pipette, then dilute to 500-ml volume with water. Do not use the reagent when it is more than 2 weeks old. Store in a brown bottle.

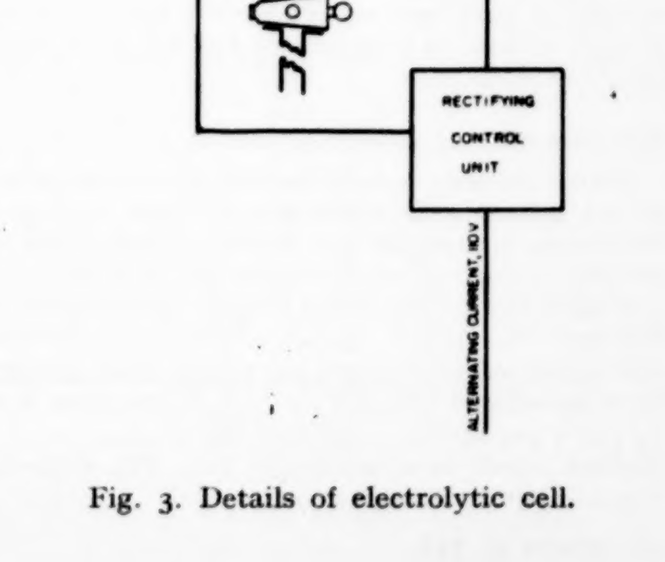
50mm BULB
25 mil TUNGSTEN WIRE LEADS
0 TO 25 MILLIAMETER
RECTIFYING CONTROL UNIT
ALTERNATING CURRENT, 110V

Fig. 3. Details of electrolytic cell.

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Amalgamated zinc, granular (or shot). Stir 400 g of 20-mesh granular zinc (or zinc shot) with 400 ml of mercuric chloride solution (5 g per 100 ml) for ten minutes. Drain off the excess mercuric chloride solution and thoroughly wash the amalgamated zinc with distilled water. (When the granular zinc amalgam has become spent it can be regenerated in places in the reducing column. Wash first with 100 ml of (1 to 4) HCl, then continue washing with distilled water until the wash water is neutral.)

Oxygen-free carrier-gas can be obtained by either of two methods:
1) Put tank helium which may contain from 2 to 20 parts per million oxygen, through a bubbler containing 200 ml of liquid NaK eutectic at a flow rate of less than 250 ml per minute. This method reduces the oxygen concentration to approximately 0.1 part per million or less.
2) Put tank hydrogen, containing 2 to 5 parts per million oxygen, through a series of three gas washing bottles (300 ml size). Each should contain 130 grams of analgamated zinc shot (see above) plus 200 ml of purifying scrubbing solution (see below). Cover each wash bottle with black tape. The effluent oxygen-concentration should be from 0.3 to 0.5 part per million.

The first method is preferable as it produces the more constant results and permits lower oxygen-concentration in the carrier gas.

Scrubbing solution, purifying grade. Dissolve 1.5 g sodium anthraquinone-beta sulfonate in 600 ml water, with gentle heat. Cool the solution to room temperature. Add 20 ml of 30 per cent sodium hydroxide, by pipette. Dilute to one liter with distilled water. This solution can be stored in a dark bottle for 60 days.

Sulfuric acid solution. Add 10 g of concentrated sulfuric acid to 90 ml of distilled water.

PROCEDURE

Assemble the system as shown in Fig. 1 with the granulated zinc amalgam in place and with freshly prepared sodium-anthraquinone-beta-sulfonate solution, analytical reagent, in reservoir bottle A. Turn stop-cock 1 so that oxygen-free carrier-gas can flow through the system. Purge the system for 10 minutes with oxygen-free gas, rotating stop-cocks 2, 3 and 4 so that the entire system is flushed with oxygen-free gas.

Preparation of the reduced analytical solution

Shut off the carrier gas, turn stop-cock 2 so that the analytical solution can flow up through the reducing column. Shut stop-cock 3 and open stop-cock 4 between the gas-scrubber and the reducing column. Raise the level of reservoir bottle A until the entire system is filled with liquid up to level C. Open stop-cock 3 and allow the analytical solution to drain back into the reservoir bottle via stop-cocks 3 and 2. Repeat this series of operations until the analytical solution is homogeneous in color and no more gas bubbles remain (3 to 5 times should be sufficient). Adjust the liquid to level D. This level should be marked, as deviation from it affects the calibration factor.

Circulation of sample gas

To start the test, turn stop-cocks 3 and 4 so that the analytical solution can circulate only through the following path: from the gas-scrubber through the gas-separator, absorption cell and back to the gas-scrubber. Turn stop-cock 1 so that the sample gas passes into the gas-scrubber through the gas-separator into the flow meter and out through the wet-test meter. Adjust the rate of gas-flow, as measured by the flow meter, so that the flow ranges from 100 to 300 ml per minute. A flow rate of 250 ml per minute is optimum for gases containing 1 part per million oxygen or less. A flow-rate of 100 ml per minute is optimum for gases containing 1 to 15 parts per million oxygen.

Determination of analytical plot

Simultaneously record the volume of gas (in liters) from the wet-test meter and the absorbance at 530 mμ with a slit-width of 0.04. Take readings at intervals of 5 to 10 minutes if the oxygen concentration is one part per million or less; take readings every one to two minutes if the oxygen-concentration is 1 to 15 parts per million.

Follow the course of analysis by plotting the absorbance as ordinate and the volume of gas as abscissa. The points should approach a straight line after a few readings. If the oxygen concentration is less than 1 part per million, continue the analysis until 10 to 20 liters of gas have been monitored and the plotted points form a straight line. If the oxygen concentration is 1 to 15 parts per million, continue the analysis until 2 to 6 liters of gas have been monitored and the plotted points form a straight line. Fig. 5 shows typical plots for analyses ranging from 0.2 to 8 parts per million.

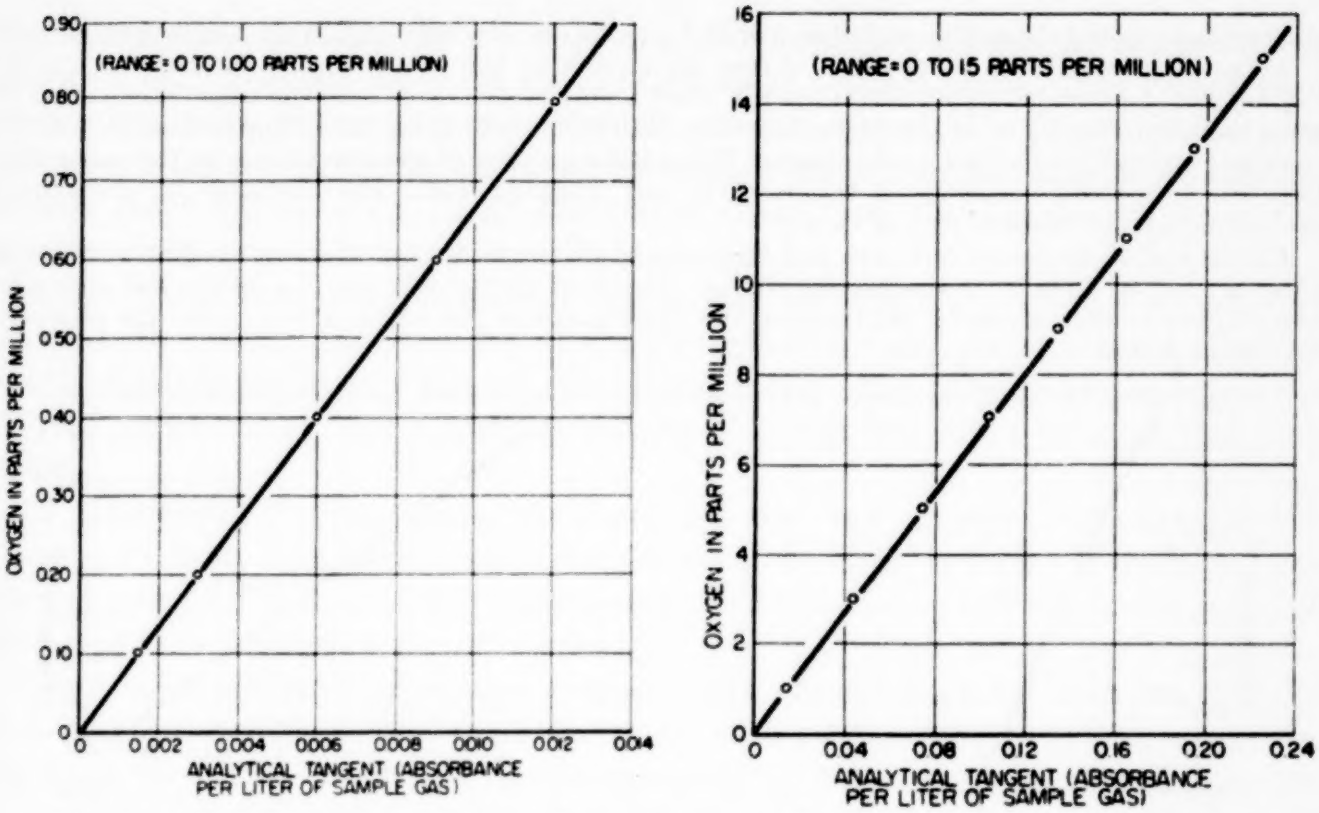

Fig. 4. Calibration curves (oxygen in parts per million *versus* analytical tangent).

Calculation of oxygen concentration

Calculate the corrected analytical tangent of the analytical plot as follows:

Analytical tangent (absorbance per liter) $= \frac{\Delta A}{\Delta V}$ . . . Eq. 1

Where ΔA = the change in absorbance observed between points A and B,

ΔV = the difference in gas volume, in liters, between points, A and B, corrected to standard conditions.

Refer to a calibration plot (Fig. 4) and read the oxygen concentration in parts per million. For example, the oxygen-concentration of sample B, Fig. 5, was calculated as follows:

$$\Delta A = 1.890\text{-}1.550 = 0.340$$

$$\Delta V = (7\text{-}0) \cdot \frac{273}{298} \cdot \frac{761}{760} = 6.4$$

$$\frac{\Delta A}{\Delta V} = \frac{0.340}{6.4} = 0.053$$

Referring to Fig. 4, the oxygen concentration is 3.5 parts per million.

Calibration curves

Connect the apparatus to a source of purified helium gas. Open stop-cock 5 and bring the level of the sulfuric acid solution to level E. Close stop-cock 5. Follow the steps as outlined for analysis of sample gas up to the point where the sample gas would be admitted to the system. At this point the homogeneous analytical solution has been brought to level D and the prepared analytical solution is isolated by stop-cocks 3 and 4. With

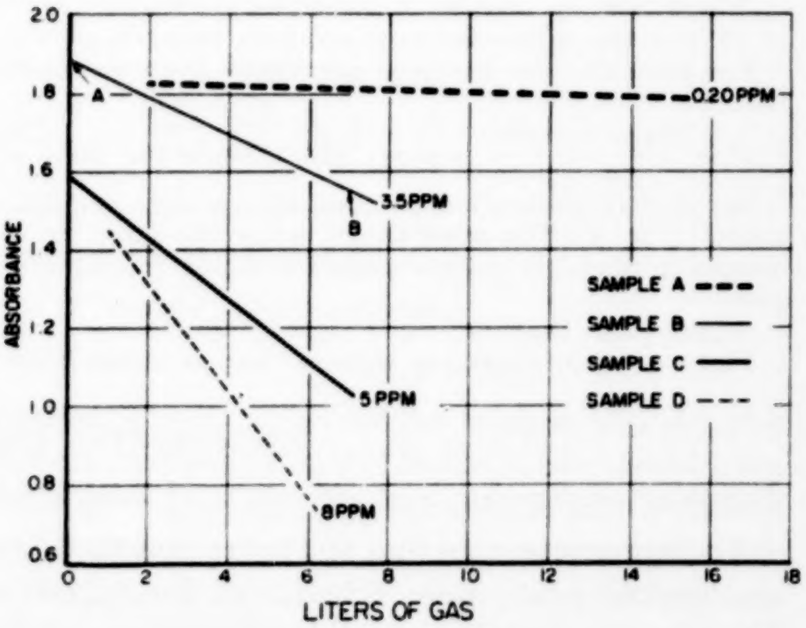

Fig. 5. Typical analytical plots.

stop-cock 1 open only to the source of purified gas, adjust the rate of flow to 100 ml per minute.

As simultaneously as is possible, throw the switch to the power-supply for the electrolytic cell, adjust the current to six milliamperes, start a stop-watch, and read the absorbance. Record absorbance at exactly 1- or 2-minute intervals. Maintain a watch on the milliammeter to secure a constant current flow of six milliamperes. Record the volume of the carrier-gas at the same time that the absorbance reading is taken. Continue readings until the decrease in absorbance levels off, approximately at 0.6 to 0.5.

Plot the absorbance as ordinate and the volume of carrier-gas as abscissa as shown in Fig. 6, Line 1. Fig. 6, Line 2, is the pre-determined blank of the carrier gas. Calculate the corrected absorbance at each point by subtracting the absorbance of the blank, line 2, from the observed absorbance, line 1.

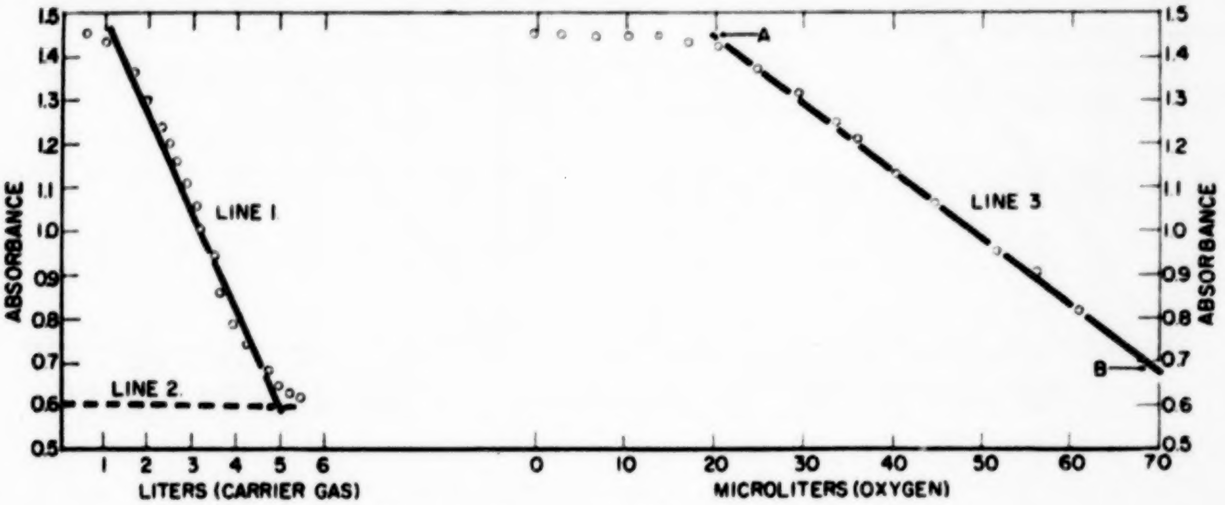

Fig. 6. Typical calibration run.

Calculate the amount of oxygen generated at a given time-interval by the following equation:

$$\text{Oxygen, in microliters} = 0.01615\, I\, t\, \frac{T}{P} \quad \ldots\ldots \text{Eq. 2}$$

Where I = the current in milliamperes which is passed through the electrolytic cell
t = the time in seconds the current flows
T = the absolute temperature during the analysis
P = the barometric pressure in millimeters.

Plot the corrected absorbance as ordinate and the oxygen generated (microliters) as the abscissa, Line 3. Calculate the calibration factor, F, from Line 3 as follows:

$$F = \frac{\Delta A^1}{\Delta V^1} \quad \ldots\ldots \text{Eq. 3}$$

Where ΔA^1 = change in corrected absorbance between points A and B
ΔV^1 = the difference in microliters between points A and B

For example, the factor is calculated from the calibration curve in Fig. 6 in the following manner.

$$F = \frac{1.452 - 0.682}{70 - 20} = 0.015 \text{ (absorbance per microliter)}$$

Set up two calibration plots as follows. One should cover the range from 1 to 15 parts per million (Fig. 4). The other should cover the range from 0 to 1 part per million (Fig. 4). The oxygen in parts per million times the factor F is equal to the corrected tangent of the analytical plot.

$$\text{"Analytical Tangent"} = F \times O_2\text{, ppm} \quad \ldots\ldots \text{Eq. 4}$$

Plot "oxygen, parts per million" *versus* "analytical tangent".

EXPERIMENTAL RESULTS

Pumping mechanism and efficiency of oxygen absorption

The apparatus was first set up as specified by BRADY[7], Fig. 2B, except that ball and socket joints were substituted for tygon joints to prevent oxygen diffusion. The pumping mechanism did not work as efficiently as expected. At the liquid-gas contact point, (Fig. 2B), where the sample gas forces the analytical reagent up through the gas scrubber, only a portion of the liquid went over the top while the majority of the liquid fell back to the liquid-gas contact point. This meant poor circulation of liquid for a given volume of gas throughput. The effects of the poor pumping efficiency could be observed visually; the color of the analytical solution became much lighter at the liquid gas contact point than it was in the gas-separator. Moreover the rate of gas-flow was highly critical.

After testing several experimental models, the dimensions given in Fig. 2A were selected. Decreasing the diameter of the bore made the gas pressure more effective in lifting all the liquid over the top. Extension of the 4-mm tube below the liquid-gas contact point meant that a greater volume of liquid was lifted for each pumping stroke.

In this model the gas forces the liquid all the way through the gas-scrubber. There is no drop-back of the analytical solution. The liquid is darker at the liquid-gas contact point than it is in the gas-separator. The flow-rate can be varied without changing the calibration factor markedly.

The greater efficiency of oxygen absorption in our modification is shown (Fig. 7) by plotting the slopes of the analytical plots, such as those shown in Fig. 4, against the parts per million oxygen of the sample gas. Fig. 7, Line 1, is calculated from our calibrations and from actual gas samples. The oxygen content of these gas samples was verified by analysis by the WINKLER method[6]. Fig. 7, Line 2, is calculated from calibration data published by BRADY[7]. Fig. 7, Line 3, is calculated from data obtained by MANN[8] using an unmodified BRADY apparatus. That our system is much more efficient can be plainly seen, since the slope of the line of a given concentration of oxygen is more than twice as great by our modification than it is by the BRADY method.

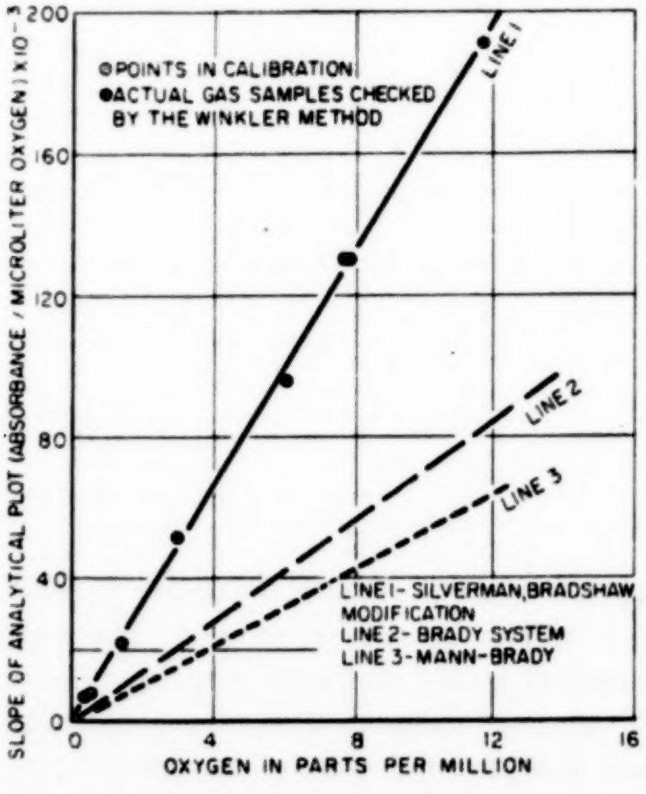

Fig. 7. Efficiency of various BRADY systems.

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Preparation of carrier-free gas

In early work the preliminary purification of helium, which averages 5 parts per million oxygen, and the purification of hydrogen, which averages 2.5 parts per million oxygen was studied, until a carrier-gas containing less than 0.5 parts per million oxygen was available.

The experimental de-oxygenation of helium and of hydrogen was first attempted using sodium anthraquinone-beta-sulfonate scrubbing solution, purifying grade. 130 g of amalgamated zinc shot plus 200 ml of scrubbing solution was optimum for each wash bottle. The results obtained in hydrogen and helium purification are shown in Table I. The lowest and most dependable results were obtained when hydrogen was put through a series of three gas-washing bottles. This type of scrubbing solution is soon exhausted and should be changed after two-weeks of exposure.

TABLE I

PURIFICATION OF CARRIER GAS USING SODIUM ANTHRAQUINONE-BETA-SULFONATE SCRUBBING SOLUTION

Gas used	*Number of gas washing bottles*	*Oxygen-concentration in parts per million*	
		Before treatment	*After treatment*
Hydrogen	3	2.5	0.1 0.1 0.3 0.3 0.4
Hydrogen	2	2.5	0.6 0.9 1.25
Hydrogen	1	2.5	1.3
Helium	3	5	0.5 0.8 1.4
Helium	4	5	1.4

In the second attempt a system of NaK bubblers produced a purer carrier gas containing 0.1 part per million or less of oxygen. The results were reproducible. The NaK bubbler, specified under reagents, can be used for helium purification until exhausted ($3.5 \cdot 10^4$ cu ft of helium). The after-treatment oxygen-concentration should remain less than 0.1 part per million oxygen.

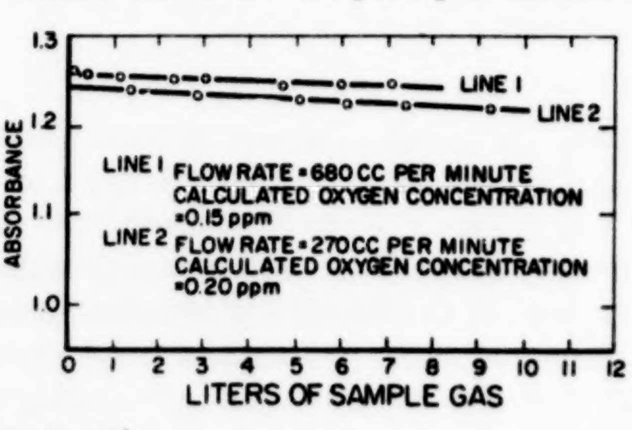

Fig. 8. Effect of flow rate on analysis.

Effect of flow-rate

The flow-rate was varied from 100 to 300 ml per minute. Such variation did not significantly affect the calibration factor or the oxygen determination. However, a slow pumping speed (100 ml per min) is preferred when the oxygen concentration is greater than one part per million, in order to obtain a smooth analytical plot.

When the oxygen concentration is less than one part per million the flow-rate can be increased to 300 ml per minute without significantly affecting the analysis. Increasing the flow-rate to approximately 700 ml per minute affects the analysis as shown by the analytical plots in Fig. 8; changing the flow-rate from 270 ml to 700 ml per minute decreased the observed concentration from 0.20 to 0.15 parts per million.

Absorbance measurements

A Klett instrument was used in the first trials. While this instrument is sensitive enough for use when the oxygen concentration is greater than one part per million, it cannot be used for lower oxygen concentrations. In order to obtain the precision and accuracy described in this paper a Beckman, model DU, spectrophotometer was used. The absorption curve is shown in Fig. 9. For our work a wave-length of 530 mμ, and a slit-width of 0.04 was selected.

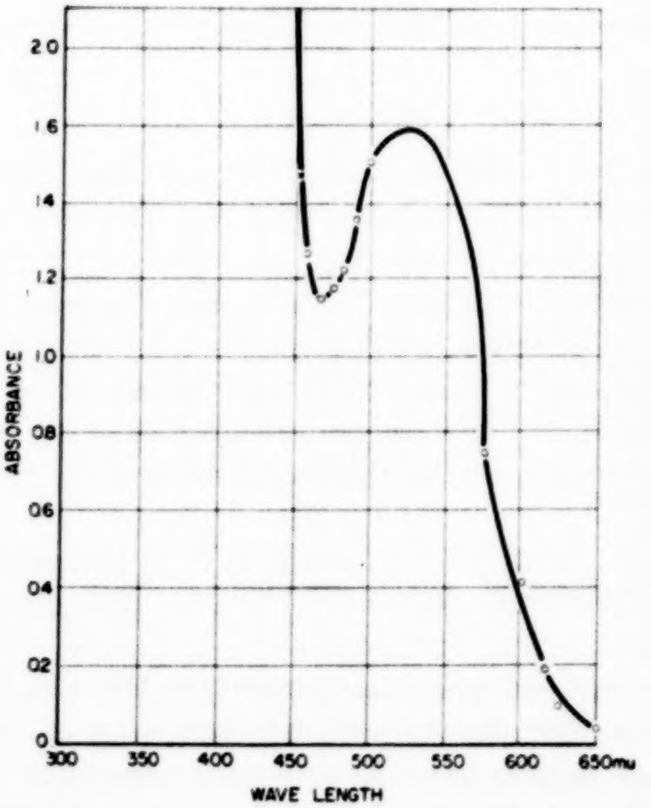

Fig. 9. Spectrophotometric curve of reduced sodium anthraquinone-beta-sulfonate.

Precision, accuracy and range of the method

The precision of the method was tested in a series of experiments using various gas samples for duplicate analyses, Table II. The standard deviation ranges from ± 0.004 part per million oxygen when the oxygen content is 0.01 part per million to ± 0.2 part per million oxygen when the oxygen content is 5 parts per million.

TABLE II

REPRODUCIBILITY OF ANALYSIS

Sample	*Oxygen in parts per million by volume*		*Standard deviation*	*Error %*
	Individual analyses	*Average*		
1	0.016 0.011	0.013	±0.004	28
2	0.023 0.017	0.020	±0.004	21
3	0.027 0.051	0.039	±0.017	44
4	0.050 0.035	0.042	±0.011	26
5*	0.103 0.113	0.108	±0.007	6.5
6	0.15 0.10	0.13	±0.04	28
7	0.26 0.28	0.27	±0.01	5
8	0.26 0.31	0.28	±0.04	13
9	0.41 0.44	0.43	±0.02	5
10*	0.60 0.70	0.65	±0.07	11
11	2.89 2.89	2.89	0.0	0
12	6.89 6.98	6.94	±0.06	1
13*	8.75 9.04	8.90	±0.21	2.3

* Samples were done on different days or at different times.

The percent error varies from 30 to 40 percent in the low range of oxygen concentration (0.01 to 0.10 part per million) through 5 to 13 percent in the median range (0.1 to 1 part per million oxygen) to 0 to 2 percent in the upper range (1 to 15 parts per million oxygen). The precision is not affected when the determinations are carried out on different days.

The accuracy of the method was checked by comparative analyses of various gas samples by the method described herein and a modified WINKLER method[6], Table III. The analyses by the two different methods do not differ from each other significantly. The two methods are calibrated by different means. The modified Brady method is calibrated by electrolytically generated oxygen, and the modified WINKLER method is calibrated by the oxidative properties of potassium dichromate. It is unlikely that

TABLE III

COMPARISON OF BRADY AND WINKLER METHODS

Sample gas	*Oxygen in parts per million by volume*			
	Brady Method (modified)		*Winkler Method*	
	Individual analysis	*Average analysis*	*Individual analysis*	*Average analysis*
Helium	6.9	6.9	6.5	6.7
	7.0		6.8	
Hydrogen	2.9	2.9	2.9	2.9
	2.9		3.0	
Purified* Hydrogen	0.4	0.2	0	
	0.0			
	0.0			
	0.3			
	0.3			

* This was purified using gas-scrubbers containing sodium-anthroquinone-beta-sulfonate, and the samples may not have been uniform.

two such widely divergent methods could exhibit the same error; therefore both methods should be accurate.

The range of the method described here-in is 0.01 to 15 parts per million oxygen. The method has been used successfully to analyse hydrogen, nitrogen, helium and argon.

DISCUSSION

A rapid, precise and accurate method is described for the analysis of micro-amounts of oxygen in hydrogen, nitrogen and inert gases. The method, a modification of that of BRADY, has a range of 0.01 to 15 parts per million oxygen.

Greater sensitivity to small amounts of oxygen is obtained by a more efficient pumping system and the use of a more sensitive photometric instrument to measure absorbance. The method is unique in being usable to measure oxygen concentrations as low as 0.01 to 0.10 part per million oxygen. The lowest concentration of oxygen detectible is 0.005 parts per million oxygen. BRADY reported a range of 1 to 100 parts per million oxygen.

The method is a dynamic one, requiring 5 to 20 liters of sample gas. However, static methods, analysing one liter of gas or less, cannot detect much less than 0.5 part per million oxygen according to PEPKOWITZ[5] and SILVERMAN AND BRADSHAW[6]. Greater reproducibility is obtained by determining the oxygen concentration from the slope of the rate of change of absorbance rather than from the difference in absorbance (BRADY's method). A double set of graphs is used to obtain the final oxygen result.

The standard deviation of the method is ± 0.004 to ± 0.04 in the low range of oxygen concentration (0.01 to 0.10 part per million oxygen), ± 0.01 to ± 0.07 in the medium range of oxygen concentration (0.1 to 1.0 part per million oxygen) and ± 0.0 to ± 0.2 in the upper range of oxygen concentration (1 to 15 parts per million oxygen). Such precision has not been attained in either dynamic or static test methods previously published. BRADY reported a precision of 5 parts per million when the oxygen concentration is 50 parts per million. PEPKOWITZ[5] reported a standard

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deviation of ± 0.8 part per million and Silverman and Bradshaw[6] a standard deviation of ± 0.3 part per million when the oxygen concentration is 1 to 30 parts per million using the static Winkler method.

The preparation of the reduced analytical solution for the modified Brady procedure is accomplished by direct mixing rather than by Brady's routine of premixing with purified carrier gas. This is desirable because our higher efficiency system is more sensitive to small amounts of oxygen than is that of Brady. Even carrier-gas containing 0.1 part per million oxygen has a noticeable blank in our improved apparatus. This use of direct mixing shortens the preparation time from 15 minutes (Brady) to 5 minutes and makes possible a more rapid determination.

The modified method is rapid, requiring one hour or less to complete an analysis. The same analysis by the Brady method would take approximately three times as long in the lower ranges of oxygen concentration. Static (Winkler) methods require at least four hours.

An improved source of oxygen-free gas containing 0.1 part per million oxygen or less is requisite to the greater precision and accuracy described.

This report is based on studies conducted for the Atomic Energy Commission under contract AT-11-1-GEN-8.

SUMMARY

The modified Brady method is a rapid one, requiring only about one hour for the analysis, but requires large samples of gas, 5 to 20 liters. The precision of the method described here-in is ±0.004 to ±0.4 in the low range of oxygen-concentration (0.01 to 0.10 part per million oxygen), ± 0.01 to ± 0.07 in the medium range of oxygen-concentration (0.1 to 1.0 part per million oxygen) and ± 0.0 to ± 0.2 in the upper range of oxygen-concentration (1 to 15 parts per million oxygen). The best precision (Winkler method) previously reported was ± 0.3 part per million oxygen. The range of the method is 0.01 to 15 parts per million oxygen. The minimum amount of oxygen detectible is 0.005 part per million.

RÉSUMÉ

Cette méthode de Brady modifiée est rapide. Une analyse ne dure qu'environ une heure, mais elle nécessite de grands volumes de gaz à analyser, 5 à 20 litres. La précision de la méthode décrite ici est: de ± 0.004 à ± 0.4 pour de faibles concentrations en oxygène (0.01 à 0.1 p.p.m.), de ± 0.01 à ± 0.07 pour des concentrations moyennes en oxygène (0.1 à 1.0 p.p.m.) et de ± 0.0 à ± 0.2 pour les concentrations les plus fortes (1 à 15 p.p.m. d'oxygène). La meilleure précision jusqu'ici signalée (méthode de Winkler) était de ± 0.3 p.p.m. d'oxygène. Le procédé décrit permet de doser des concentrations en oxygène de 0.01 à 15 p.p.m. La quantité minimum d'oxygène décelable est de 0.005 p.p.m.

ZUSAMMENFASSUNG

Die hier beschriebene Modifikation der Brady'schen Methode is rasch, denn für eine Analyse genügt eine Stunde, sie erfordert aber grosse Gasproben (5 bis 20 Liter). Die Genauigkeit dieser Methode beträgt ± 0.004 bis ± 0.4 für niedrige Sauerstoffkonzentrationen (± 0.01 bis 0.1 p.p.m.), ± 0.01 bis ± 0.07 für mittlere Sauerstoffkonzentrationen (0.1 bis 1 p.p.m.) und ± 0.0 bis ± 0.2 für die höchsten Konzentrationen (1-15 p.p.m. Sauerstoff). Die bis heute beste Präzision wurde für die Winkler'sche Methode aufgeführt und betrug ±0.3 p.p.m. Sauerstoff. Die beschriebene Methode erlaubt Sauerstoffkonzentrationen von 0.01-15 p.p.m. zu bestimmen. Die kleinste, bestimmbare Menge Sauerstoff beträgt 0.005 p.p.m.

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SÉPARATION Rb-Cs PAR CHROMATOGRAPHIE SUR CELLULOSE EXTRACTION SÉLECTIVE DU ^{137}Cs DE FISSION

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INTRODUCTION

Dans le cadre du programme de recherches sur la séparation des produits de fission de l'uranium, nous avons recherché, d'une part, une méthode microchimique de séparation chromatographique Rb-Cs sur cellulose et d'autre part, une méthode d'extraction aussi rapide que possible du césium de fission, „carrier free".

Ces deux éléments sont d'importants produits de fission et tout spécialement ^{137}Cs (33 ans) offre des perspectives d'applications industrielles intéressantes[1,2].

Le problème de la séparation chromatographique Rb–Cs a été abordé déjà par d'autres auteurs[3,4,5] qui se plaçaient, sauf en ce qui concerne LEDERER, du point de vue de la simple séparation et de l'identification des alcalins entr'eux.

Dans cette étude, nous nous sommes limités à la méthode de séparation chromatographique sur cellulose.

PRODUITS — MESURES

a. *Papiers*: Pour les essais sur bandes de papier, nous avons utilisé le Whatman no. 1; les bandes ont 1 cm de large et environ 20 cm de longueur utile.
Les expériences sur colonne ont été effectuées au moyen de poudre de cellulose Whatman grade B, purifiée suivant le procédé décrit dans une publication antérieure[6].

b. *Radioisotopes*: Nous disposions pour la mise au point et l'application des procédés préconisés des produits suivants:
1. ^{86}RbCl (19.5 j.), en provenance de Harwell, produit par activation neutronique.
2. ^{137}Cs (33 a.) de fission, en provenance de Harwell; il contient également un peu de ^{134}Cs (2.3 a.).
3. ^{134}Cs (2.3 a.) extrait du RbCl activé à la pile de Harwell (impureté).
4. U irradié à la pile de Harwell durant un mois; nous disposions de deux échantillons: le premier a été utilisé six mois après l'irradiation (Uranium A); le second seulement quarante jours après la fin de l'irradiation (Uranium B).
Nous nous plaisons à remercier M. H. HUBERT, directeur au centre des applications de l'énergie nucléaire, qui a eu l'amabilité de mettre ces échantillons à notre disposition.

c. *Mesures*: La détection sur bande de papier a été faite généralement par mesure d'activité au compteur G.M.; dans certains cas, cependant, nous avons été obligés d'utiliser la détection chimique au cobaltinitrite de sodium.
Pour les essais sur colonne, les différentes fractions recueillies au moyen d'un appareil automatique sont généralement évaporées en cuvette et les concentrations sont déterminées par

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mesure de l'activité du résidu. Dans certains cas, nous avons dosé le rubidium par spectrophotométrie de flamme, après dilution par 3 à 4 volumes de méthanol (λ = 7800 Å).
Enfin, dans un cas, nous avons simplement déterminé le pic du rubidium par pesée du résidu d'évaporation de RbCl; il s'agissait d'une expérience d'extraction du césium d'un échantillon de RbCl irradié à la pile.

ESSAIS DE SÉPARATION CHROMATOGRAPHIQUE Rb-Cs

1. Élution au mélange méthanol-HCl 12N

Nous avons commencé par essayer l'élution chromatographique au moyen de mélange méthanol-HCl 12*N* qui s'est avéré très efficace pour la séparation des alcalino-terreux et satisfaisante pour celle de Li, Na, K.

Ces essais ont été faits sur une colonne de cellulose de 9 mm de diamètre intérieur et de 20 cm de haut, à la température constante de 18° C. Nous avons essayé des éluants contenant, pour 100 volumes de méthanol, 0 à 5 volumes de HCl 12*N*. Les résultats sont donnés dans la Fig. 1; elle situe le début, le maximum et la fin (caractérisée par le dixième du maximum) des pics du rubidium et du césium. On peut voir que la séparation est pratiquement nulle dans tout le domaine exploré.

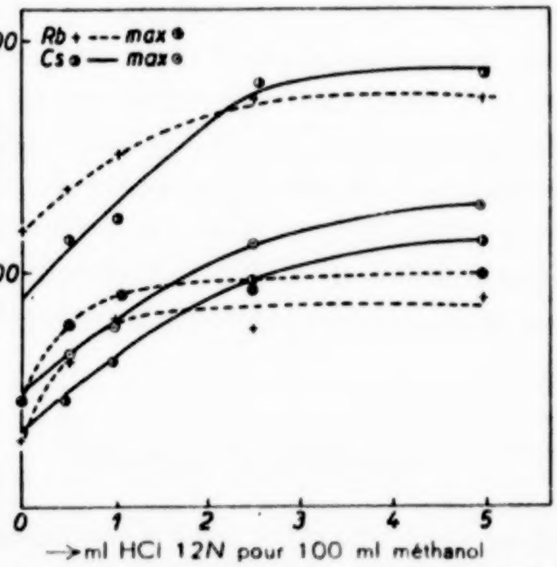

Fig. 1. Essais de séparation chromatographique sur colonne de cellulose au moyen d'éluants à base de méthanol et de HCl 12*N*.

Nous n'avons pas jugé utile de poursuivre ces essais avec des éluants plus riches en acide chlorhydrique d'autant plus qu'avec des mélanges contenant du méthanol et de l'acide chlorhydrique en parts à peu près égales, on observe une inversion dans l'ordre des élutions: le césium migre plus rapidement que le rubidium et le potassium[3].

D'autre part une trop forte concentration en acide chlorhydrique désagrège assez rapidement la cellulose.

2. Recherche d'un nouvel éluant

Nous avons procédé à des essais d'orientation sur bandes de papier avec différents solvants; les quantités de Rb et Cs mises en oeuvre dans chaque essai étaient de l'ordre de 100 à 200 γ et la révélation se faisait au cobaltinitrite.

Les Tableaux I et II résument les résultats obtenus:

TABLEAU I

ÉLUANTS A BASE DE MÉTHANOL

Éluant	*Volumes*			R_F *de* Rb^+	R_F *de* Cs^+	$p = \frac{R_F Cs}{R_F Rb}$
	A	*B*	*C*			
Méthanol pur				0.26	0.25	1
Méthanol (A)	100	1	5	0.14	0.17	
HCl 12*N* (B)			10	0.22	0.18	
H_2O (C)			20	0.38	0.36	1
			50	0.55	0.55	
			100	0.65	0.65	
	100	0.1	10	0.33	0.33	1
			20	0.43	0.43	
Méthanol (A)	100	1		0.2	0.2	1
HNO_3(conc.) (B)		0.1		0.2	0.2	
Méthanol (A)	100	1		0.12	0.12	1
$HClO_4$(conc.) (B)		0.1		0.2	0.2	
Méthanol (A)	100	1		0.23	0.23	1
Acide acétique glacial (B)		0.1		0.22	0.25	
Méthanol (A) Acide monochloracétique (B	100	(10 g)		0.32	0.30	1
Méthanol (A) NH_4Cl (B)	100	(saturé)		0.2	0.2	1
Méthanol (A)	100	2		0.2	0.2	1
NH_4OH aq. (B)	$CsNO_3$ $RbNO_3$			0.29	0.26	
Méthanol (A) Phénol (B)	100	(10 g)		0.28	0.28	1

TABLEAU II

ÉLUANTS DIVERS

Éluant	*Volumes*		R_F *de* Rb^+	R_F *de* Cs^+	$p = \frac{R_F Cs}{R_F Rb}$
	A	*B*			
Pyridine pure			0.07	0.07	1
Pyridine (A) H_2O (B)	100	20	0.15	0.15	1
Morpholine (A)	100	0	0	0	1
H_2O (B)		15	0.25	0.25	
Acétylacétone	équilibrée avec HCl 6*N*		0	0	
Phénol	équilibré avec HCl aq. 20 % (v/v)		0.31	0.56	**1.8**
Acétone (A) HNO_3 conc. (B)	100	5	0.07	0.07	1

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On constate que seul l'éluant à base de phénol, déjà proposé par STEEL[4] et utilisé par LEDERER[5] donne une différence de R_F suffisante et des taches bien localisées.

Nous avons ensuite voulu nous rendre compte si le phénol équilibré avec HCl 2*N* pouvait également convenir pour une séparation sur colonne; ces essais ont été effectués au moyen d'une colonne thermostatisée à 18° C, de 1 cm de diamètre et contenant une hauteur de cellulose de 8 cm (2.5 g de cellulose); par essai, la quantité de RbCl utilisée était d'environ 10 mg et celle de CsCl beaucoup plus faible ($\leqslant 50\ \gamma$).

La Fig. 2b reproduit l'une des courbes d'élution obtenue dans une série de quatre essais consécutifs destinés à éprouver la reproductibilité de la méthode; les quatre chromatogrammes étaient superposables.

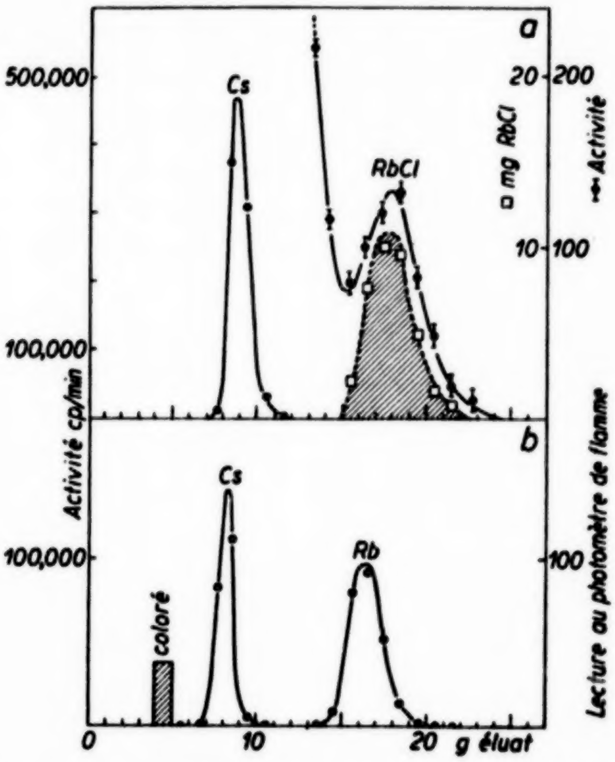

Fig. 2a et 2b. Séparations chromatographiques Rb-Cs sur colonne de cellulose par élution au moyen de phénol équilibré avec HCl 2*N*.

Notons que le pic du césium a été déterminé par mesure d'activité (^{134}Cs) tandis que celui du rubidium a été relevé au spectrophotomètre de flamme. La séparation sur colonne est excellente: l'activité de la cuvette située deux places avant celle où l'on commence à détecter le rubidium, représente $\frac{2}{10.000}$ de l'activité totale du césium.

Le volume libre de la colonne est de l'ordre de 4 g d'éluant; on peut l'apprécier grâce à la coloration brunâtre du petit volume de phénol qui a servi à amener les produits sur la colonne; ce volume était de 0.5 ml et il se retrouve dans la 5e fraction.

3. *Application*

Nous avons eu l'occasion de vérifier l'intérêt de cette méthode en radiochimie; nous disposions de RbCl irradié à Harwell (^{86}Rb: 19.5 j.), qui après décroissance presque complète du rubidium, gardait une activité parasite très importante; nous l'avons soumis à une chromatographie, à la fois sur bande de papier et sur colonne.

Après une mise en équilibre de la colonne avec le phénol équilibré avec HCl 2*N*, nous y avons versé 1 ml d'une solution saturée du RbCl impur dans l'éluant ($\sim$ 40 mg de RbCl): la Fig. 2a

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montre le chromatogramme obtenu: un pic intense à la place du césium (environ 750.000 cps/min): les mesures d'absorption et de décroissance cadrent également avec cette attribution; le chlorure de rubidium utilisé pour l'irradiation contenait des traces de césium qui ont été également activées en donnant du ^{134}Cs (2.3 a.). Cette même remarque a été faite récemment par d'autres auteurs[7].

Les fractions d'élution contenant normalement le chlorure de rubidium ont été recueillies dans des cuvettes en verre; après évaporation de l'éluant, le résidu a été pesé (voir la courbe d'élution en hachuré; il est d'ailleurs à noter que ce rubidium possède encore une très faible activité dont la courbe concorde bien avec celle déterminée par gravimétrie).

On voit ainsi que le procédé chromatographique sur colonne est intéressant non seulement du point de vue analytique mais également d'un point de vue préparatif: il peut convenir parfaitement pour préparer du chlorure de rubidium exempt de césium destiné à une irradiation ou si l'on veut, pour purifier le chlorure de rubidium activé: la chose est d'autant plus intéressante que la période du ^{86}Rb est relativement courte vis-à-vis de celle du césium d'activation.

Si l'on désire contrôler rapidement la pureté radiochimique d'un échantillon de RbCl d'activation, un chromatogramme sur bande de papier est tout indiqué.

La Fig. 3 montre le résultat obtenu avec le même échantillon de RbCl: *a* est un témoin obtenu avec 100 γ de CsCl marqué avec ^{137}Cs; *b* est le chromatogramme du RbCl de Harwell quelques mois après l'irradiation: l'essai d'activité montre à nouveau l'existence du césium: la position du rubidium a été déterminée au cobaltinitrite et vérifiée par mesure d'activité (voir *c*).

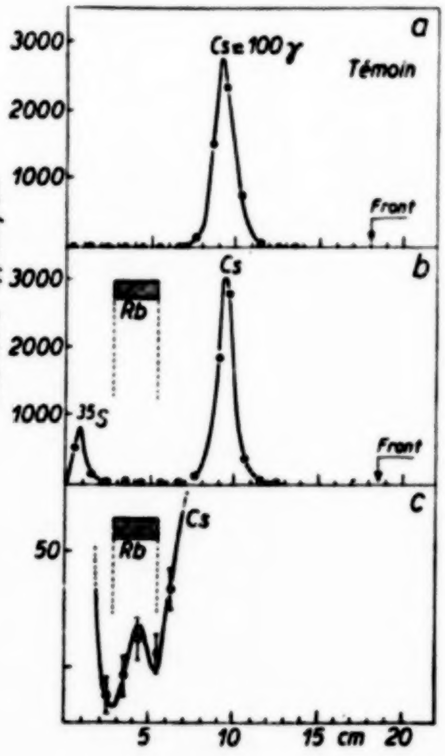

Fig. 3. Chromatogramme sur bande de papier de RbCl irradié à Harwell. Élution au phénol équilibré avec HCl 2*N*.

Il est intéressant de constater qu'il existe encore une certaine activité près de l'origine: il s'agit d'un radioélément d'une période de l'ordre de 90 jours et de très faible énergie (E_{max} = 0.14 à 0.17 Mev.); il s'agit vraisemblablement de ^{35}S (87.1 j.; E_{max} = 0.167 Mev.) produit par une réaction (n,p) sur le ^{35}Cl de RbCl[8].

EXTRACTION DU ^{137}Cs DE FISSION

Le césium est un des produits de fission de longue période et une méthode d'extraction de ce produit à l'état „carrier free", par un procédé simple, serait intéressante.

Quelques essais préliminaires nous ont rapidement montré que le phénol équilibré avec HCl 2*N* semble parfaitement convenir: Sr^{+2}, Ba^{+2}, Ce^{+3}, terres rares, Pb^{+2}, Pd^{+2}, Sn^{+2} ne s'éluent pratiquement pas; au contraire pour I^- et Sb^{+3}, on obtient des R_F respectivement de 0.1 et 0.35. I et IO_3^- (réduit au contact de l'éluant) migrent avec un R_F voisin de l'unité; cet „iode" n'est plus extractible par CCl_4.

Signalons que dans l'uranium irradié durant un mois à la pile, on retrouve, six mois après la fin de l'irradiation, principalement les émetteurs β suivants avec leurs contributions approximatives au rayonnement[9] suivantes:

^{144}Ce (^{144}Pr): 40%; ^{91}Y: 20%; ^{90}Sr (^{90}Y): 20%; ^{95}Zr (^{95}Nb): 10%;
^{103}Ru-^{106}Ru (^{106}Rh): 4%; ^{137}Cs : 2%; Te : 1%.

Ceci nous a amené à essayer immédiatement un chromatogramme sur la solution nitrique d'uranium irradié (Uranium A).

1. Essais sur bandes de papier

a) Éluant: phénol équilibré avec HCl 2N

Lors du premier essai (Fig. 4c), nous avons été surpris de constater la présence d'une activité relativement importante de R_F voisin de 1; elle est accompagnée d'une intense coloration brune formée à l'origine, quand le phénol entre en contact avec la tache de départ.

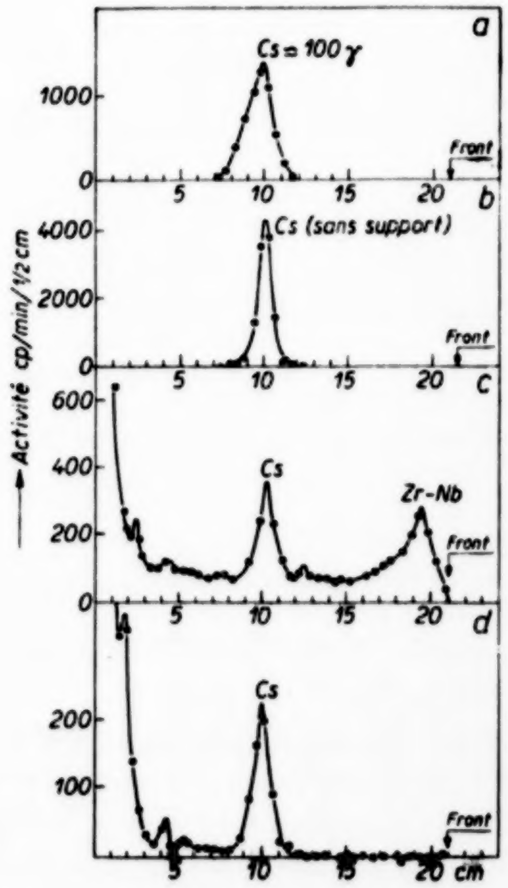

Fig. 4. Chromatogramme sur bande de papier d'uranium irradié à la pile. Élution au phénol équilibré avec HCl 2*N* (six mois après la fin de l'irradiation).

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Cette activité parasite semble avoir laissé une traînée plus ou moins constante tout au long du chromatogramme et l'activité β représente environ 10% de l'activité totale des produits de fission restant à l'origine; cela nous fit supposer que nous étions en présence de ^{95}Zr (colloïdal?). Des essais ultérieurs ont confirmé cette attribution.

La plus grosse partie de l'activité β (Ce, Y, Sr) reste à l'origine: on observe néanmoins un léger pic qui se situe vers $R_F = 0.1$. Nous avons trouvé qu'il s'agissait du ruthénium: ^{103}Ru et ^{106}Ru (+ ^{106}Rh de filiation).

Enfin, au milieu du chromatogramme, on observe le pic de ^{137}Cs qui se détache nettement sur le fond continu; la concordance avec un échantillon de ^{137}Cs „carrier free" élué simultanément est frappante (Fig. 4b). Lorsqu'on y ajoute 100 γ d'entraîneur inactif, le pic devient un peu plus large (Fig. 4a).

Nous avons réussi à nous débarrasser de l'action gênante du zirconium, soit en déposant sur la bande de papier une goutte d'eau oxygénée (à 30 volumes) à l'endroit où sera mise la solution ($\sim 3 \mu l$) contenant l'uranium et les produits de fission, soit en exposant le papier après chargement de la solution à séparer à des vapeurs de sulfure d'ammonium.

La Fig. 4d montre le résultat obtenu par traitement avec H_2O_2.

b) Éluant: phénol équilibré avec H_2O

Les résultats sont très similaires (Fig. 5): le R_F de Cs^+ n'a pratiquement pas varié mais le pic est un peu plus large. Près de l'origine, le pic de Ru se détache mieux ($R_F = 0.14$).

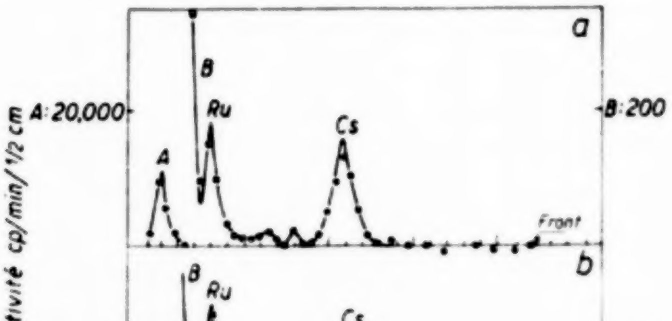

Fig. 5. Chromatogramme sur bande de papier d'uranium irradié à la pile. Élution au moyen de phénol équilibré avec l'eau (six mois après la fin de l'irradiation).
a) Phénol éq. H_2O; bande traitée par H_2O_2.
b) Phénol éq. H_2O.
c) Phénol éq. H_2O; origine traitée par $(NH_4)_2S$.

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Dans ce cas, même sans traitement du papier [H_2O_2 ou vapeur de $(NH_4)_2S$], nous n'avons plus observé de radioélément s'éluant plus vite que le césium.

Dans l'ensemble des essais effectués sur bandes de papier, nous avons constaté que l'activité du pic de Cs^+ représente en moyenne 2.2% de l'activité totale, valeur en accord avec les données de la littérature.

On voit ainsi qu'au moyen du phénol équilibré avec HCl 2*N* ou H_2O, il est possible d'éluer sélectivement le césium de la solution d'attaque de l'uranium contenant tous les produits de fission. Cette méthode est extrêmement rapide et fournit un produit très pur.

Nous avons encore voulu nous rendre compte si le procédé reste aussi sélectif lorsqu'on part d'uranium fraîchement retiré de la pile; à cet effet, nous avons utilisé l'uranium B (voir p. 527). L'essai a été fait sur bande de papier traitée au préalable avec H_2O_2.

Un des chromatogrammes obtenus est représenté dans la Fig. 6. Par suite de l'activité élevée de cet uranium, nous avons été obligés de découper l'origine de la bande où était concentrée la majeure partie des radioéléments de fission, pour pouvoir obtenir des mesures correctes des activités relativement faibles réparties le long du chromatogramme (Fig. 6b). On observe néanmoins, en plus du pic de ^{137}Cs (comparé au témoin de la Fig. 6a) un pic supplémentaire au front de l'éluant.

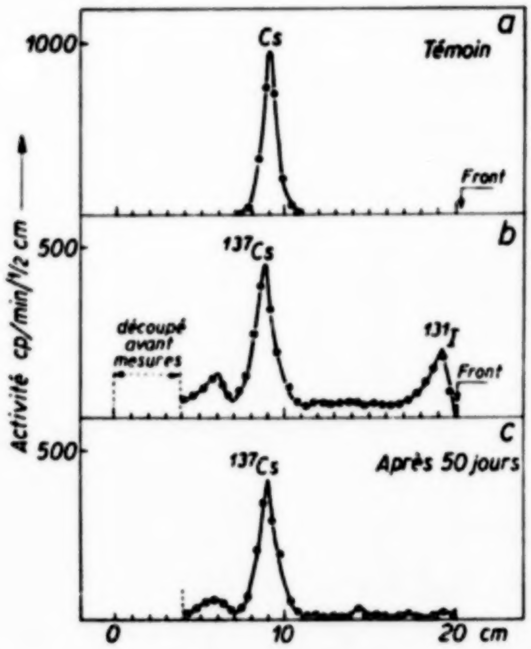

Fig. 6. Chromatogrammes sur bandes de papier d'uranium irradié à la pile. Élution au moyen de phénol équilibré avec HCl 2*N* (quarante jours après la fin de l'irradiation).

Les mesures de décroissance et d'absorption nous ont montré qu'il s'agit en majeure partie de ^{131}I (période 8 j.; $E_{max} = 0.6$ Mev.). Sur la Fig. 6c se trouve le même chromatogramme mesuré 50 jours plus tard, après la décroissance presque complète de ^{131}I.

Le petit pic situé à gauche de celui de Cs^+ (Fig. 6b et 6c) n'a pas encore été identifié; il se pourrait que ce soit ^{125}Sb, puisque nous avons trouvé que son R_F est de l'ordre de 0.35.

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2. *Essai sur colonne de poudre de cellulose*

L'expérience a été faite sur une colonne de 8 cm de longueur et de 1 cm de diamètre. La température est maintenue constante à 18° C; l'élution se fait au moyen de phénol équilibré avec HCl 2*N*.

Après la mise en régime de la colonne avec l'éluant, on y introduit une petite goutte de la solution nitrique d'uranium irradié (uranium A) et l'on commence l'élution.

Sur le chromatogramme de la Fig. 7a, on remarque la présence d'une importante activité juste après la sortie du premier volume libre, en même temps que la coloration brune intense formée au départ au contact de la solution nitrique.

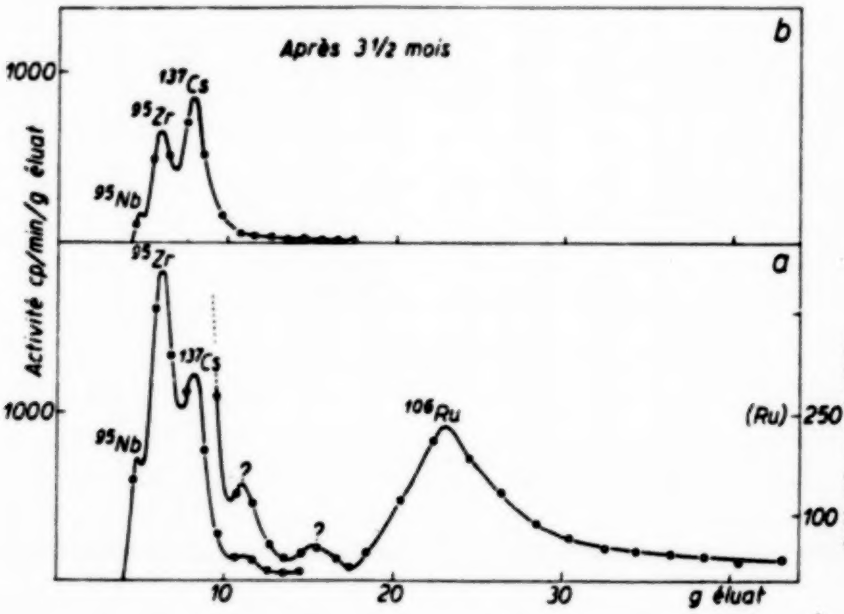

Fig. 7. Chromatogramme sur colonne de cellulose de l'uranium irradié à la pile (six mois après la fin de l'irradiation). Élution au phénol équilibré avec HCl 2*N*.

Cette activité ne pouvait manifestement pas être due uniquement au ^{137}Cs dont le maximum se situe vers deux volumes libres.

L'examen des décroissances des portions initiales, ainsi que des mesures d'absorption nous ont conduit aux attributions suivantes:

le premier pic est dû surtout à ^{95}Nb (35 j.),
le deuxième à ^{95}Zr (65 j.),
le troisième à ^{137}Cs à la place attendue (Fig. 7b.).

Cette dernière figure nous montre la répartition des activités (Ru excepté) $3^1/_2$ mois plus tard.

Un dernier pic étalé, a été attribué au ^{106}Ru + ^{106}Rh (et évidemment ce qui reste de ^{103}Ru), en effet:

i. C'est le seul radioélément qui, parmi les produits de fission susceptibles de se trouver en quantité notable à ce moment, ait une énergie de rayonnement β aussi élevée: 3.5 à 3.9 Mev. (due au ^{106}Rh, filiation de ^{106}Ru, de période 30 s.).

ii. D'autre part, une fraction notable ($> 30\%$) de l'activité a pu être distillée „carrier free" après oxidation par $KBrO_3$. Les portions non distillées ont pratiquement la même énergie de rayonnement.

iii. Enfin la période trouvée est de l'ordre de l'année (^{106}Ru, période: 1 a.).

Si, avant de mettre les produits sur la colonne, on y laisse tomber quelques gouttes d'eau oxygénée à 30 volumes, on observe de nouveau, comme sur bande de papier, le pic très net du ^{137}Cs, suivi de celui du ruthénium (Fig. 8). On observe néanmoins, avant le pic du césium, une très petite activité qui n'a pas été identifiée; il ne s'agit certainement pas d'une anomalie dans le pic de ^{137}Cs car nous avons observé une décroissance nette après deux mois.

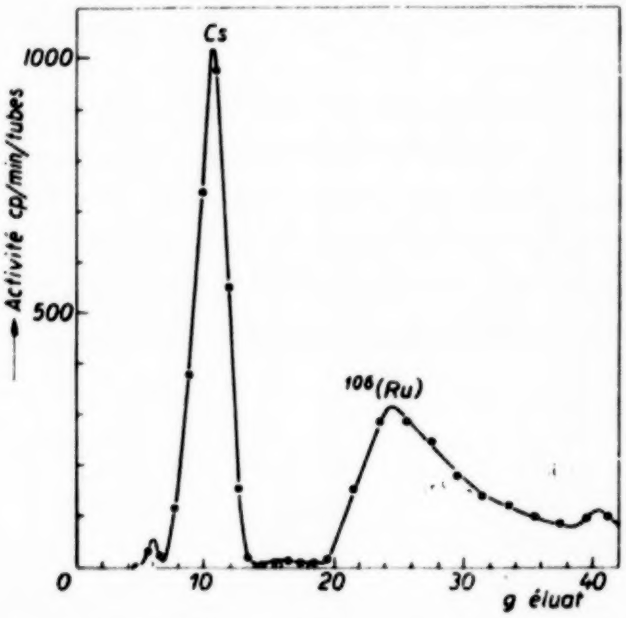

Fig. 8. Même essai que dans la Fig. 7. Traitement avec une goutte d'eau oxygénée.

REMERCIEMENTS

L'un de nous (J. F.) se plaît à remercier Messieurs les professeurs G. GUEBEN et G. DUYCKAERTS pour l'intérêt qu'ils ont porté à ce travail, Monsieur J. GOVAERTS pour l'assistance dans les mesures d'absorption et l'Institut des Sciences Nucléaires pour les subsides qu'il a bien voulu nous accorder.

RÉSUMÉ

La recherche d'une bonne méthode de séparation Rb-Cs, en quantités microchimiques par chromatographie sur cellulose, nous a montré que seul un éluant à base de phénol (équilibré avec H_2O ou HCl $2N$) permet d'obtenir, de façon simple, des résultats excellents.

Cette séparation reste excellente aussi bien avec des quantités de quelques milligrammes qu'avec des doses extrêmement faibles et nous avons pu l'appliquer à la séparation sélective du ^{137}Cs de fission „carrier free", directement à partir d'une solution nitrique d'uranium irradié.

SUMMARY

A search for a good method of separating Rb-Cs in micro-quantities by chromatography on cellulose has revealed that only with a phenolic eluant (equilibrated with H_2O or $2N$ HCl) can a specially good separation be easily obtained.

This separation remains quite effective from quantities of a few milligrams to "tracer" amounts, and we were able to obtain a selective separation of fission ^{137}Cs "carrier free", directly from a nitric solution of irradiated uranium.

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ZUSAMMENFASSUNG

Auf der Suche nach einer guten mikrochemischen Trennungsmethode von Rb-Cs mittels Chromatographie auf Zellulose hat es sich gezeigt, dass nur Elution mit Phenol (das mit H_2O oder 2*N* HCl gesättigt ist) eine besonders gute Trennung ergibt.

Diese Trennung bleibt sowohl mit Mengen von einigen Milligrammen als auch mit Spuren sehr gut. Es gelang uns, nach dieser Methode das Spaltprodukt ^{137}Cs aus einer bestrahlten Urannitratlösung selektiv abzutrennen.

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ELECTRO-CHROMATOGRAPHY AND THE MOVEMENT OF COMPLEX IONS

by

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Much study has been devoted to the electro-chromatography of inorganic cations since the technique was first recorded in 1951. Separations of many groups of cations have been attempted and several papers have been devoted to examining the factors controlling the movement of inorganic ions during electro-chromatography.

LEDERER AND WARD[1,2] investigated the movement of a large number of metal ions using hydrochloric acid as the carrier electrolyte. The differential movement was attributed to capillary flow of the solvent in the paper, adsorption on the paper and the potential applied. The movement of individual ions was greatly influenced by the concentration of HCl used as the carrier, since for metals which form complexes with chloride ions, the mobility of the ion may change with the chloride concentration.

SATO, NORRIS AND STRAIN[3] examined the electro-chromatographic sequences of inorganic cations with a large variety of electrolytic solutions and found that the sequences were dependent upon the composition of the electrolytic solution and upon the nature and treatment of the porous support. The mechanisms of these variations could be related to many effects, such as the formation of complexed ions in the electrolytic solution, variation of the sorption of ions by the porous support and variation of the activity or degree of dissociation of the migrating ions.

The electro-osmotic flow of liquid which occurs in paper electro-chromatography was investigated by ENGELKE, STRAIN AND WOOD[4] and was attributed to a driving force within the paper. This force was found to depend upon the electrical field, the treatment of the paper and the concentration and nature of the electrolytic solution. The electro-osmotic flow increased with increasing field strength and dilution of the electrolytic solution, and under the conditions employed in these experiments, the electro-osmotic migration exceeded the electrical mobilities of many ions. Thus the mobilities and even the direction of migration of substances examined by electro-chromatography cannot be accurately specified unless the electro-osmotic transport is determined or controlled. Since electro-osmosis is a function of many variables, these authors were pessimistic regarding the possibility of obtaining precise, reproduceable values for the mobility of ions.

The effect of concentration and sorption upon the migration of cations has recently been studied by SATO, NORRIS AND STRAIN[5]. With zones of ions such as Pb and Bi, that are readily sorbed by the paper, the rate of electrical migration was found to be proportional to the concentration and approaches an upper limit as the concentration of the ion approached the ionic concentration of the back-ground electrolytic solution on the paper. Similar results were obtained with comparative paper chromatograms with variation of cation concentration. Many ions, particularly those not sorbed by the paper, migrated at a rate independent of their concentration provided that the concentration was less than that of the electrolytic back-ground solution. With zones of the mixture at concentrations higher than that of the electrolytic solution, the migration decreased with increasing concentrations. At the leading boundaries of the zones, the ions diluted by diffusion and convection migrate rapidly, producing long diffuse leading regions.

The conclusions of these detailed American studies confirm in many respects the validity of the interpretations published by LEDERER AND WARD in the earlier studies. In paper electro-chromatography, the separability of mixtures of various ions depends upon the differential migration rates. These rates have been shown to vary with many conditions such as the nature and concentration of the back-ground electrolytic solution moistening the paper, the treatment and wetness of the paper, the temperature, magnitude of the osmotic effect, the concentration and sorbability of the ion. Since several of these factors are difficult to control in analytical studies, the ideal condition for separations involves the formation of at least one ion of opposite electrical sign to other ions present.

This condition may be obtained by electro-chromatographing mixtures of complex ions. The stability of the complex could have a profound influence on both the type and charge of ion attracted by the applied potential and the sorption of ions by the paper could vary between complex and simple salts.

We have studied the movement of metal nitrates on paper moistened with potassium nitrate under varying conditions of relative concentration, in order to make a preliminary study of the analytical possibilities of separations through added complex ions.

EXPERIMENTAL

The glass-plate technique recorded by Lederer and Ward was adopted using Whatman No. 120 Spot Reaction Filter Papers and either molar, deci-molar, or centi-molar KNO_3 as the carrier electrolyte on the paper. The ends of the paper not enclosed by the glass plates dipped into reservoirs of the carrier electrolyte and a potential equivalent to 5 volts/cm of paper was applied for seventy minutes through two carbon electrodes immersed in the reservoirs.

With the dilute carrier solutions little heating was observed but with the molar carrier cooling of the glass plates was found desirable.

M, *M*/10 and *M*/100 solutions of the nitrates of Ag, Pb, Hg, Bi, Cd, Cu, Fe, Mn, Ni and Co were prepared and approximately 0.004 ml quantities were spotted in the centre of the filter paper and the relative rates of movement and size of resultant spots were compared using different concentrations of carrier electrolytes.

Complex ions of the metals were formed by diluting the molar nitrates to deci-molar with excess of the following reagents: NH_4OH, alkaline KCN, KCNS, weakly acid and weakly alkaline solutions of disodium ethylenediaminetetraacetate. Spots of these solutions (including precipitates formed) were treated similarly to the nitrates using 0.1*M* KNO_3 as carrier electrolyte.

Where necessary, complex ions were decomposed by spraying with acid before the cations were finally located with H_2S and other standard spot test reagents.

The results of the practical experiments are summarized in Tables I and II. The ionic movements tabulated were obtained by measuring the distance between the centre of the original spot and the centre of the spot located after electro-chromatography. In many cases ionic movement was accompanied by diffusion and expansion of the zone size and an indication of the increase in size is given by the numbers in parentheses shown on the tables. These numbers represent the approximate multiple increase and in the majority of expansions, the original circular area (of approx. 50 sq. mm) was greatly elongated in the direction of the flow of ions.

The approximate spot areas are considered to be so important that they cannot be overlooked when using ionic movement for the purposes of predicting analytical separations since with large areas, one particular cation can be found in many positions on the paper and will readily interfere with other ions of larger or smaller ionic mobility, thus preventing clear boundaries.

Occasionally, complexing agents formed precipitates on the addition of the cation and this fact is recorded in Table II. In some cases cations from the precipitated material moved completely during electro-chromatography while other compounds gave two spots implying that two species existed in the complexed solution.

Under the standard conditions used in this experiment, the degree of reproducibility of results was highly satisfactory and the figures recorded are the mean values of several tests.

DISCUSSION

Nitrates were chosen as the anion for the metals and carrier electrolyte since they were believed to have a minimum tendency to form anionic complexes in simple salt solutions. Under the comparative conditions of the electro-chromatograms the variation in movement of the simple cations could thus be attributed to the major influence of a single factor such as increased diffusion with dilute carrier electrolytes or increased sorption with decreasing concentration of cation present.

Electro-osmotic flow has been shown to increase with increasing dilution of carrier electrolyte[4] and the variation in cation movement with increasing flow is shown by the horizontal rows of figures in Table I. From these results it may be tentatively concluded that direct flow of solvent has had little effect on actual forward movement of the cations but the flow has assisted the difusion of the soluble metal salts. The more dilute the carrier, the greater the tendency for the cations under test to diffuse throughout the solution. This diffusion will give the equivalent of low concentrations of cation over wider surfaces of paper which may facilitate greater adsorption and explain the smaller movement observed for most ions in 0.01M KNO_3 carrier solutions. The increased diffusion is readily discerned by comparing the relative spot areas of similar amounts of metal salt in different carrier electrolytic solutions. The diffusion of the metal salt into the carrier would be retarded by having a higher concentration of salt in the carrier as is shown by the results tabulated in Table I.

Previously reported acceleration[2,4] did not occur and ionic mobility was influenced more by the secondary effects of diffusion.

Other workers[2,5] have emphasized the important role of sorption on the movement of inorganic ions and their conclusions have been confirmed by our study. Some ions such as Ag^+, Pb^{+2}, Bi^{+3}, Hg^{+2} and Fe^{+3} are strongly sorbed by the paper and their movement is largely dependent on the concentration of cation present. Paper, like other adsorbents may be considered capable of adsorbing different quantities of material per unit weight of paper. Where adsorbing capacity for a metal is high, *e.g.* Bi^{+3} and Hg^{+2}, the original spot remains unmoved even at high concentrations. Where adsorbing capacity is smaller, high concentrations of a cation may move under the influence of the electrical field until the dilution is sufficiently great to allow complete adsorption over a wider area. This effect is shown by Ag^+ and Pb^{+2}. Some ions are apparently little adsorbed and have similar migration under all conditions *e.g.* Mn^{+2}, Ni^{+2} and Co^{+2}. With high concentrations of carrier electrolyte,

TABLE I

THE EFFECT OF VARIATIONS IN THE CONCENTRATION OF CARRIER ELECTROLYTE AND METAL SALT ON THE MOVEMENT OF CATIONS

Spotted salt	*Concentration of KNO_3 carrier*			*Remarks*
	molar	*0.1 molar*	*0.01 molar*	
M $AgNO_3$	+38 mm (13)	+39 mm (13)	+24 mm (17)	The spots which moved were comet shaped, tailing back to zero. With *M* $AgNO_3$ much Ag^+ was concentrated at the leading edge.
0.1*M* ,,	+11 ,, (2)	+17 ,, (6)	+13 ,, (4)	
0.01*M* ,,	+2 ,, (1)	0 ,, (1)	0 ,, (1.5)	
M $Pb(NO_3)_2$	+21 ,, (4)	+31 ,, (13)	+25 ,, (18)	Diffuse and cometed spots were obtained when the $[Pb^{+2}]$ > the molarity of the carrier electrolyte
0.1*M* ,,	+12 ,, (3)	+14 ,, (4)	+15 ,, (11)	
0.01*M* ,,	+2 ,, (1)	+27 ,, (2)	+9 ,, (4)	
M $Hg(NO_3)_2$	+8 ,, (4)	+11 ,, (5)	+13 ,, (5)	The ions adsorbed strongly on the paper but some movement occurred when $[Hg^{+2}]$ > the KNO_3 molarity
0.1*M* ,,	+8 ,, (3)	+1 ,, (2)	+5 ,, (3)	
0.01*M* ,,	0 ,, (1)	0 ,, (1)	+2 ,, (2)	
M $Bi(NO_3)_3$	0 ,, (1)	+2 ,, (2)	+2 ,, (2)	The bismuth salt was very strongly adsorbed by the paper
0.1*M* ,,	0 ,, (1)	0 ,, (1)	0 ,, (1)	
0.01*M* ,,	0 ,, (1)	0 ,, (1)	0 ,, (1)	
M $Cd(NO_3)_2$	+36* ,, (6)	+18 ,, (7)	+26 ,, (22)	High concentrations of Cd salt diffused over broad areas extending from the original spot
0.1*M* ,,	+50* ,, (9)	+15 ,, (4)	+30 ,, (6)	
0.01*M* ,,	+49* ,, (1)	+14 ,, (2)	+30 ,, (2)	
M $Cu(NO_3)_2$	+27 ,, (3)	+30 ,, (10)	+24 ,, (21)	Similar to $Pb(NO_3)_2$
0.1*M* ,,	+21 ,, (3)	+26 ,, (4)	+17 ,, (7)	
0.01*M* ,,	0 ,, (1)	+27 ,, (1)	+11 ,, (2)	
M $Fe(NO_3)_3$	+7 ,, (4)	+16 ,, (9)	+4 ,, (2)	The iron was strongly adsorbed by the paper and observed migration was due to tailing from the original spot
0.1*M* ,,	+13 ,, (3)	+1 ,, (2)	+4 ,, (2)	
0.01*M* ,,	+1 ,, (1)	+2 ,, (1)	+0 ,, (1)	
M $Mn(NO_3)_2$	+40* ,, (1)	+30 ,, (2)	+32 ,, (11)	The cations migrated in fairly compact zones
0.1*M* ,,	+44* ,, (6)	+30 ,, (1)	+36 ,, (2)	
0.01*M* ,,	+48* ,, (1)	+26 ,, (1)	+37 ,, (1)	
M $Ni(NO_3)_2$	+27 ,, (6)	+26 ,, (11)	+23 ,, (19)	The Ni^{+2} migrated as elongated ovals extending from above the original spot
0.1*M* ,,	+26 ,, (4)	+27 ,, (4)	+20 ,, (14)	
0.01*M* ,,	+22 ,, (1)	+30 ,, (1)	+18 ,, (4)	
M $Co(NO_3)_2$	+40* ,, (7)	+30 ,, (2)	+27 ,, (16)	
0.1*M* ,,	+52* ,, (8)	+29 ,, (2)	+34 ,, (8)	Similar to nickel
0.01*M* ,,	+52* ,, (2)	+29 ,, (1)	+26 ,, (3)	

* Heating effects may have influenced the movement of these ions.

The results in parentheses represent the approximate increase in area of spot caused by electrochromatography

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TABLE II

THE EFFECT OF COMPLEXED FORMS ON IONIC MOVEMENT

Metal	*Aqueous nitrate*	*Complexing agent present*				
		Alk. KCN	*KCNS*	*NH_4OH*	*EDTA*	
					pH 3	*pH 9*
Ag	+17 mm (6)	−22 mm (1)	0* mm (1)	+22 mm (7)	0* & −8 mm	−12* mm (7)
Pb	+24 ,, (4)	0* ,, (1)	+24* ,, (4)	+15* ,, (2)	5* & −15 ,,	−20 ,, (2)
Hg	+1 ,, (2)	−12 ,, (3)	−8* & 0 mm	0* ,, (2)	* − 2 ,,	0* & −17mm
Bi	0 ,, (1)	0 ,, (1)	0 mm (1)	0* ,, (1)	0 & − 3 mm	−10 mm (5)
Cd	+15 ,, (4)	−7 ,, (2)	+15 ,, (4)	+8 ,, (1)	+8 & − 9 ,,	+6 & −10mm
Cu	+26 ,, (4)	−24 ,, (1)	+22 ,, (1)	+16 ,, (1)	+9 & − 13mm	0 & −20 ,,
Fe	+1 ,, (2)	0* & −45 mm	+4 ,, (2)	0* ,, (1)	0 mm (1)	−15 mm (7)
Mn	+30 ,, (1)	−11 mm (2)	+28 ,, (2)	+11 ,, (2)	+5 ,, (1)	0 ,, (1)
Ni	+27 ,, (4)	−37 ,, (7)	+33 ,, (7)	+15 ,, (2)	+17 ,, (5)	+24 ,, (8)
Co	+29 ,, (2)	−28 ,, (4)	+21 ,, (8)	+4 ,, (3)	+18 ,, (8)	+6 ,, (4)

* Indicates that a precipitate was present in the spotted solution.

The carrier electrolyte was 0.1 M KNO_3 and the concentration of metal ions in the spot solution was 0.1 M.

there is obviously a "salting effect" which decreases the solubility of small quantities of metal ions and thus increases the absorption (*cf.* 0.01 M Ag^+, Cu^{+2} and Fe^{+3} on M KNO_3 carrier). Conversely, high concentrations of carrier electrolyte will tend to reduce the adsorptive capacity of unit area of paper and hence concentrated solutions of cations will be free to move with less retardation due to sorption and under ideal conditions may move as concentrated zones.

The effects of complex ions on the movement of cations was studied by spotting the complex (in the presence of a small excess of reagents) directly on the paper. This technique was considered preferable to that of SATO, NORRIS AND STRAIN[3] in which the complexing agent was used as the carrier. The latter method has the advantage of ensuring the presence of complexing agent at all times and hence equilibrium will favour the continued existence and movement of a metal complex. It has been shown[6,7] that in simple chromatographic separations, the degree of movement and size of spot can be proportional to the relative concentration of cation and complexing agent unless the latter is present in large excess. Thus for uniform migration, a concentrated solution of complexing agent is desirable. This could lead to heating of the paper due to high current flow. Heating would increase liquid flow and ionic mobilities.

The addition of the complexed salt to a neutral carrier involves effects due to the different stabilities of compounds. Indications from the preliminary studies shown in Table II are that the stabilities of complexes during electro-chromatography can be different from those anticipated from standard figures of stability constants.

The anionic cyanide complexes of Ag, Cu, Ni and Co all moved similar distances while the weaker complexes of Hg, Cd and Mn were transported less than half the distance of the very stable complexes.

In the presence of KCNS, Hg^{+2} was the only cation which tended to move as an anionic complex. With the exception of silver (precipitate of AgCNS), the movements observed with other cations were almost identical with the behaviour of the simple nitrates under similar conditions.

Of the amine complexes, silver amine moved slightly more than the simple ion probably due to a reduced tendency for sorption while the movement of the amines of Cu, Cd, Ni and Co were appreciably smaller. Since the effect was much larger with Co, this retardation could be attributed to the smaller charge per unit area of the co-ordinate complex molecule.

Complexes of cations and di-Na ethylenediaminetetraacetate are usually very stable but it is recorded[8] that the stability can be influenced by the ionic strength of the solution and the pH of the solution. The instability brought about by this salt effect in electro-chromatograms is clearly illustrated by the figures in Table II. Many cations yielded double spots, one anionic (the complex) and one cationic (the simple ion). Normally, all the cations tested form strong anionic complexes with EDTA but it will be observed that two of the most stable, *viz.* Ni and Co, are apparently completely decomposed and only the simple cation is attracted by the applied potential. The resultant spots are very diffuse but the total movement is only slightly less than that of the similarly treated simple salt.

Thus while the formation of complex ions may be used to separate cations which tend to react from those that do not (using the technique of SATO[3]), further investigation of the "salting effect" as shown in EDTA solutions may lead to separations within a complexed group.

CONCLUSIONS

The investigation has confirmed that the movements of inorganic cations during electro-chromatography are influenced by the concentration and type of cations present, the concentration of carrier electrolyte, the temperature and sorptive capacity of the paper for the cation.

The results obtained place a slightly different emphasis on the role of the carrier electrolyte. This electrolyte can reduce the migration by "salting out" small concentrations of cations or increase the movement by occupying active centres on the paper thus reducing sorption of the cation by the paper. Dilute carrier solutions promote electro-osmotic flow in the paper and allow concentrated test spots to diffuse over large areas. In the presence of complex ions, the ionic strength of the carrier may be sufficiently great to cause decomposition of otherwise stable ions.

SUMMARY

It is apparent that, in electro-chromatographic separations, the change of area undergone by the initial spot of test solution plays a part in the final interpretation of results almost as important as the actual movement of the centre of the spot.

Several interesting facts have emerged from this research concerning the role of the carrier electrolyte on the movement, the spot size, and the stability of complex salts.

RÉSUMÉ

Il ressort que dans les séparations électrochromatographiques, le changement de l'étendue de la tache initiale d'une solution à examiner joue un rôle dans l'interprétation finale des résultats, presque aussi important que celui du mouvement même du centre de la tache.

Ces recherches mettent en évidence plusieurs faits intéressants, concernant l'influence de l'électrolyte de base sur le mouvement, les dimensions de la tache et la stabilité des sels complexes.

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ZUSAMMENFASSUNG

Es ist augenscheinlich, dass bei elektrochromatographischen Trennungen, die Oberflächenänderung des ursprünglichen Flecks der Testlösung bei der Endauslegung der Ergebnisse eine beinah ebenso wichtige Rolle spielt, wie die Wanderung des Fleckmittelpunktes selbst.

In dieser Untersuchung treten verschiedene interessante Tatsachen hervor, die sich auf die Wirkung des Trägerelektrolyten auf die Wanderung, Fleckgrösse und Beständigkeit der komplexen Salze beziehen.

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INORGANIC ANALYSIS IN ORGANIC SOLVENTS

I. SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM FOLLOWING A CHROMATOGRAPHIC SEPARATION

by

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INTRODUCTION

Whereas several cations have been determined spectrophotometrically by measurement of the colour intensities of their 8-hydroxyquinolates in organic solvents[1-5], no similar method for the determination of chromium has been reported. Chromium forms a yellow 8-hydroxyquinolate and 8-hydroxyquinaldate* that are not easy to precipitate quantitatively from pure chromium solutions and which possess spectral properties similar to those of several other such metal complexes and to those of the reagents themselves.

This paper describes a method in which the 8-hydroxyquinolate, or better, the 8-hydroxyquinaldate complexes of chromium are separated from those of most other metals by selective adsorption on activated alumina from organic solvents, especially benzene-chloroform 1:1 solutions. The chromatographic column is unelaborate, and is rapidly prepared. After separation, the chromium is determined by measuring the optical density of the solution at the adsorption maximum of the complex employed. The solutions of both complexes obey the Beer-Lambert law. Essentially the method is micro, but to avoid sampling errors, *e.g.*, where comminution of the sample is difficult, it is necessary to take macro starting weights and obtain the determination sample by taking a suitable aliquot. The method is applicable to the determination of chromium in a very wide range of materials, including ferrous and non-ferrous alloys, chromium ores and other mineral matter. The chromium, unless present only as a very minor constituent, may be determined to within ± 0.2 μg, *i.e.*, to within about 1 part in 200 in the average case.

Organo-chromium complexes do not readily and quantitatively form conveniently filterable precipitates, and the 8-hydroxyquinaldate is considerably more difficult to collect than the 8-hydroxyquinolate[6]; but in the presence of sufficient ferric iron chromium is precipitated quantitatively and in an easily filterable condition by either complexing agent. The amount of iron present in the precipitation solution must be at least twice the amount of chromium, and should also be at least equal to the combined weights of all other metals. Those metals which form crystalline complexes, *e.g.*, cobalt and nickel, inhibit rather than assist the complete precipitation of chromium. In the case of ferrous alloys and iron ores, sufficient iron is present for all the chromium to be precipitated, but in some other cases, addition of about 5 mg of ferric iron is necessary before precipitation.

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* The term "8-hydroxyquinaldate" (*cf.* 8-hydroxyquinolate) is used to describe the complexes of 8-hydroxyquinaldine, in order to avoid confusion with quinaldinates, the salts of quinaldinic acid.

References p. 552.

Because of the relative ease of precipitation, 8-hydroxyquinoline is recommended as the better reagent provided that aluminium, cobalt and vanadium are absent: the 8-hydroxyquinolates of these three metals are not completely retained on alumina from benzene-chloroform 1 : 1. Vanadium and aluminium, however, cause no difficulties when present only in relatively minor amounts. Cobalt and pentavalent vanadium are completely retained on alumina when 8-hydroxyquinaldine is used as reagent, but tetravalent vanadium is not, and interferes in the spectrophotometric determination of chromium. Special circumstances arise when only small amounts of chromium are present in the presence of much vanadium, as for example in the analysis of ferrovanadium. In this case, both vanadium and chromium are oxidized by digestion with ammonium persulphate, the excess of persulphate being destroyed by further boiling. The small amount of dichromate is reduced by and combines with the 8-hydroxyquinaldine, while all the vanadium remains in the pentavalent state. The digestion time must be extended by 10-20 minutes in this case; the oxidation products of the reagent appear to have no adverse affect on the analysis.

Since 8-hydroxyquinaldine does not react with aluminium, this metal will, when present, appear in the precipitate as its hydrated oxide and efforts should be made to remove excessive amounts of this element before the solution is made ammoniacal, otherwise the bulky hydrated oxide is an inconvenience. Tartaric acid must not be added to prevent precipitation of hydrated alumina because it also prevents complete precipitation of chromium.

The developing solvent, benzene-chloroform 1 : 1, or when fire hazards preclude the use of benzene, trichloroethylene-chloroform 1 : 1, is chosen so that all the chromium appears in the eluate and all other metals, apart from known interferences, are retained in the column. Chromium is completely retained on alumina from pure benzene or trichloroethylene, while some other metals are not completely retained from pure chloroform[7]. Alcohol dissolves traces of alumina from the column, but the small percentage of alcohol used as a preservative in the chloroform has no adverse affect, and, indeed, it must not be removed, otherwise the photochemically produced hydrogen chloride decomposes the organo-metallic complexes, and low results are obtained in the chromium determination.

EXPERIMENTAL PROCEDURE

(i) *Size of the sample*

The amount of chromium which is passed through the column should be between 0.01 and 0.3 mg (the extreme lower limit is about 2 μg, but the chromium can only be measured to within ± 0.2 μg; the upper limit may be raised to 0.6 mg by diluting the eluate to 100 ml instead of 50 ml). The total weight of metals to be adsorbed on the column should be between 1 and 5 mg, although up to 10 mg can be handled by using longer columns. In some cases, such as ferrous alloys and iron ores, which contain sufficient iron to co-precipitate the chromium, a sample weight containing 5 mg of metals may be taken provided that sampling errors are avoided and the chromium content is not above 10%; all the sample is precipitated and passed through the column. The taking of aliquots is recommended in the following circumstances: (a) when comminution of the sample is impossible, or segregation is significant, (b) when the chromium

content is above 10% so that a 3-5 mg sample contains more chromium than may be passed through a column. In this case, an aliquot is taken of the aqueous solution and ferric iron is added before precipitation.

If the alloy is mainly iron and very low in chromium, a much larger sample may be taken, and most of the iron removed by ether extraction from a solution 6*N* with respect to hydrochloric acid[8]. In the case of non-ferrous alloys, the sample weight must be chosen, bearing in mind the smallest weight representative of the whole, the expected chromium content and the amount of iron to be added.

(ii) *Attack of the sample*

(a) *Alloys not attacked by alkalies*

Cover the sample with water, add 5-20 ml of dilute (1:1) sulphuric acid and warm gently to dissolve the metal. If the attack is very slow (as with nickel alloys), add 10 ml of concentrated hydrochloric acid to speed dissolution, but chloride ions must be removed by evaporation to fuming before the addition of oxidizing agents in order to avoid losses as chromyl chloride; then dilute to 20-30 ml with water. Add 10 ml of concentrated nitric acid, evaporate to fumes of sulphuric acid, cool, dilute to 20-30 ml with water and warm gently until all metal-salts have dissolved. If resistant carbides are present, fuming with sulphuric-perchloric acid may be necessary: if this is done, boil the solution for ten minutes after dilution of the residue. If the ferric concentration is excessive, make 6*N* with respect to hydrochloric acid by adding an equal volume of the concentrated acid and extract once with an equal volume of ether. Boil off the ether from the aqueous layer before precipitating the organic complexes. Sufficient ferric ions remain to ensure complete precipitation of the chromium complexes.

(b) *Aluminium and other alloys attacked by aqueous alkali*

If the alloy is rich in aluminium, zinc or other metal which dissolves in alkalies (or water), cover the sample with hot water and add 10% sodium hydroxide, a little at a time, until the metal is completely attacked. The weight of sample must be chosen according to the proportion of alkali-insoluble metals. Filter off the alkali-insoluble residue which invariably contains all the chromium; wash with 1% sodium hydroxide and then with water. Dissolve the residue in 20 ml of dilute (1:5) sulphuric acid, with additions of concentrated nitric acid if necessary. The solution is evaporated to fuming and the filter paper is destroyed by further small additions of nitric acid, and the fuming is continued to remove traces of volatile mineral acids.

(c) *Ores, Minerals, etc.*

Many minerals such as haematite and carbonates may be partially attacked with dilute (1:1) hydrochloric acid, those rich in silica should be attacked with hydrofluoric-nitric acid mixture. Any residue which cannot be attacked by acids must be fused with five times its weight of sodium peroxide in an iron crucible. This procedure is the only one suitable for attacking chromite unless it is virtually free from silica, when perchloric acid may be employed[9]. When the fusion method of attack is used, leach out the fused cake with water after cooling, and acidify with sulphuric acid. In those cases where a wet attack is possible, all hydrofluoric and nitric acids must be removed by fuming with 10 ml of sulphuric acid.

(iii) *Reduction of Cr^{VI} to Cr^{III}*

The solution to be precipitated with 8-hydroxyquinoline or 8-hydroxyquinaldine must not contain appreciable amounts of chromate or the chromium will not be precipitated quantitatively. In those cases where all the chromium is oxidized to the hexavalent state, as when fuming with perchloric acid or fusion with sodium peroxide are necessary, the chromate is reduced by boiling the resulting dilute sulphuric acid solution with 5 ml of alcohol for 15 minutes.

(iv) *Precipitation of the organic complexes*

The total weight of metals present in the solution should be 3-5 mg (excluding aluminium) or 10-50 mg if an aliquot is to be taken of the chloroform solution. Dilute the solution, if necessary, to 20 ml, heat to 70° C and add dilute (1:1) aqueous ammonia drop by drop, with stirring, until a faint permanent precipitate is formed; dissolve this with a drop of dilute sulphuric acid and proceed as follows:

(a) 8-Hydroxyquinoline as reagent: add 10 ml each of 2% 8-hydroxyquinoline in 2*N* acetic acid, *N* sodium hydroxide and 4*N* ammonium acetate in that order, with continuous stirring.

These quantities of reagents are sufficient for up to 10 mg of metals of average atomic weight 50 and valency 2-3, and proportionately more should be used for larger amounts. Adjust the pH to 8 by the addition, drop by drop, of dilute (1:1) aqueous ammonia, boil for one minute, digest with occasional stirring for ten minutes, or until the precipitate is coagulated and the liquid clear yellow.

(b) 8-Hydroxyquinaldine as reagent: prepare a diluted reagent solution by taking a volume of 2% 8-hydroxyquinaldine in 2*N* acetic acid such that there is an excess of 1-2 ml over the amount required to combine with all the metals present, and dilute to 10 ml (or 20 ml) with 2*N* acetic acid. If a larger excess is used, the reagent separates as an oil, causing the precipitate to become pasty, in which case all the chromium is not precipitated. Add the diluted 8-hydroxyquinaldine solution to the weakly acid solution of the metals, followed by 10 ml (or 20 ml) each of *N* sodium hydroxide and 4*N* ammonium acetate with stirring. 10 ml quantities of reagents are sufficient for up to 10 mg of metals (excluding aluminium); 20 ml should be used for larger amounts. Adjust the pH to 6 by the addition, drop by drop, of dilute ammonia or sulphuric acid and digest the solution at 70-80° C, with frequent stirring, until the precipitate has coagulated and the liquid is clear yellow.

Collect the precipitate in a sintered glass crucible and wash it with 20-30 ml of hot water. It is unnecessary to transfer quantitatively the adhering precipitate from the beaker to the filter. A Schwarz-Bergkampf type filter beaker of 100 ml capacity, if available, is most convenient, thus enabling the precipitation, and solution of the complexes in chloroform to be carried out in one vessel. Dry the crucible and beaker at 105-110° C.

Dissolve an 8-hydroxyquinaldate precipitate by drawing 20-30 ml of hot chloroform through the crucible, wash the beaker with chloroform and combine the solutions. As 8-hydroxyquinolates do not dissolve so readily, transfer these precipitates to the precipitation beaker, wash the crucible with 40-50 ml of hot chloroform and add this to the beaker containing the precipitate. Keep the mixture hot until all the solid has dissolved. Examination over an intense light source is a suitable means of observing when solution is complete. If an aliquot is to be taken of the chloroform solution, dilute it, when cold, to exactly 100 ml with chloroform.

(v) *Preparation of the chromatographic column*

(a) Tube to hold the alumina column

The tube should be 5-6 mm internal diameter, about 30 cm long, with a wider portion at the top so that it will hold at least 30 ml above the alumina. A ground glass joint just above the stopcock is desirable to facilitate cleaning. The spring-loaded stopcock barrel must be of good quality and should be lightly smeared with silicone grease.

(b) Preparation of the column

Pour 5 ml of benzene-chloroform (1:1) into the tube, push a piece of cotton wool down to the bottom of it with a glass rod, and fill it with the solvent mixture to the top of the narrow part. If the tube has aquired an electrostatic charge, place a concentric wider tube over it. Pour in sufficient dry, dust-free sand through a long funnel to form a layer 1 cm deep on top of the cotton wool, followed by a quantity of activated alumina, as the dry powder, sufficient to form a column 4 cm high. When the alumina has settled, add a second, similar quantity. The tube should be tapped gently after each addition of sand or alumina to level the top of the column. The layer of fines in the middle of the alumina column so formed ensures retention of traces of any complexes, except chromium, which may pass the top of the column. A column 8 cm high is sufficient for up to 20 mg of complexes; proportionately longer columns are necessary for larger amounts.

(vi) *Chromatographic separation and determination of chromium*

If the whole of the chloroform solution of the precipitate is to be passed through the column, evaporate it to 10-12 ml. If the weight of precipitate exceeds 50 mg, evaporate to 30 ml. In either case add an equal volume of benzene. Alternatively, take a 10 ml aliquot from 100 ml and add 10 ml of benzene. Mix well, run the liquid out of the column, leaving 1 cm above the alumina and add the solution of the metallic complexes; rinse the beaker with the solvent mixture and add the washings to the column. Place a clean, dry 50 ml or 100 ml graduated flask beneath the column (the 100 ml flask is necessary when the volume of chloroform solution of the complexes exceeds 12 ml, and when more than 0.1 mg of chromium is present as its 8-hydroxyquinolate), open the stopcock and let the liquid run into the flask at a rate not exceeding one drop per second. As soon as all the liquid has passed through, wash the column with benzene-chloroform (1:1) until the flask is full to the mark. Stopper the flask and mix well. Measure the optical density of the yellow solution spectrophotometrically at 425 mμ (8-hydroxyquinolate) or 410 mμ (8-hydroxyquinaldate). Choose the path length according to the colour-intensity of the solution.

(vii) *Standards*

Prepare a standard chromic solution from A.R. potassium dichromate or electrolytically refined chromium metal. To various aliquots of this solution add 10-20 mg of iron as ferric sulphate solution and proceed exactly as described above for both reagents. Plot graphs of optical density against mg of chromium in 50 or 100 ml, which will be straight lines from zero to as far as it is possible to measure optical densities accurately.

DISCUSSION

Interferences and sources of error

To obtain accurate results, two conditions must be fulfilled:

(a) All the chromium in the aqueous solution must be precipitated as the organic complex. This is ensured by having sufficient ferric iron present and at least most of the chromium in the trivalent state, and by using the correct excess of reagent.

(b) All the chromium must elute from the column, and all the other metals must be completely retained on it.

All the chromium will elute, if the right proportions of benzene and chloroform are used. For most activated alumina, a 1 : 1 mixture by volume is satisfactory. The metals which are not completely retained on the column under the conditions of the determination are as follows:

8-Hydroxyquinolates: aluminium and vanadium (except in very minor amounts) and cobalt cause high results. Aluminium 8-hydroxyquinolate is not completely retained on activated alumina from 1 : 1 benzene-chloroform and causes a marked interference on account of its bright yellow colour and strong fluorescence. It is also formed if 8-hydroxyquinoline is passed through the column. Owing to the alcohol present in commercial chloroform, any vanadium 8-hydroxyquinolate will be present in the red form[10]. This is not adsorbed on alumina, and may elute as a red solution if present in large amount; but in contact with alumina, it decomposes, forming an aluminium 8-hydroxyquinolate. Anhydrous cobalt 8-hydroxyquinolate is completely retained on the alumina column, but its dihydrate is not adsorbed at all. But even when dehydrated at 120° C, sufficient moisture is always present in the solvents to cause at least a partial re-formation of the dihydrate.

8-Hydroxyquinaldates: of the metals investigated, namely Fe^{III}, Al, U, Ce, Ti, Ni, Cu, Mo, Mn, Co, Th, Zn, V^{V}, W, Ga, In, Tl, and alkaline earths, none have been found to cause any interference in the chromium determination. Aluminium does not form an 8-hydroxyquinaldate, and the cobalt derivative is completely retained in the column, probably because it does not form a hydrate. The 8-hydroxyquinaldate of pentavalent vanadium does not form a red coloured solution with the amount of alcohol present in commercial chloroform, and it is completely retained on alumina with no apparent decomposition. However, all the vanadium must be in the pentavalent state, as the 8-hydroxyquinaldate of tetravalent vanadium is only weakly adsorbed on alumina, and would consequently cause high results.

Results — Accuracy and precision

The following tables illustrate the wide range of materials and chromium concentrations which can be analysed by the above method.

(a) *8-Hydroxyquinoline as reagent*

Material		*Analytical results %*	*Mean %*	*Chromium by standard methods %*
Ferrochromium	BCS 203	69.2, 69.4, [illegible], 69.0	69.3	69.0
Cr-V Steel	BCS 165	0.87, 0.85, 0.89, 0.90	0.87	0.86
Cr-Ni-Ti Steel	BCS 209	18.30, 18.25, 18.26	18.3	18.7
Cr-Ni Steel	BCS 189	0.69, 0.65, 0.68	0.67	0.68
Cr-Ni-Mo Steel	BCS 219	0.82, 0.82, 0.83	0.82	0.82
Co-V Steel	BCS 167	6.69, 6.81	6.75	3.32
Co-V Steel	BCS 167	3.33, 3.30	3.32*	3.32
Cr-V-W-Co Steel	BCS 166	7.01, 7.08	7.04	3.01
C Steel	BCS 163	0.029, 0.027	0.028	0.03
Alloy Cast Iron	BCS 173	3.90, 3.81	3.86	3.97
Alloy Cast Iron	BCS 172	0.385, 0.392	0.39	0.41
Cr-V Steel	BCS 224	1.61, 1.57	1.59	1.46
Low Alloy Steel	BCS 257	1.71, 1.71	1.71	1.72
Inconel		13.5, 13.5	13.5	14.0
Brightray		20.6, 20.9	20.7	21.0
Hydra 80-20		20.20, 20.35	20.3	20.5

* Figure obtained after group separation of the cobalt.

(b) *8-Hydroxyquinaldine as reagent*

Material		*Analytical results %*	*Mean %*	*Chromium by standard methods %*
Ferrochromium	BCS 204	71.3, 71.1	71.2	71.4
Kanthal		23.8, 24.0	23.9	23.3
Cobalt Steel	BCS 167	3.20, 3.38	3.29	3.32
Haematite		2.38, 2.33	2.36	2.38
Chromite		30.73, 31.20, 30.94	31.0	30.90
Aluminium Alloy		0.077, 0.074, 0.075	0.075	0.07
Aluminium Alloy		0.020, 0.019, 0.020	0.020	0.02
Ferrovanadium		0.073, 0.078	0.075	—

The analytical results given in the above tables are those of determinations on true replicates on the original sample, duplicate aliquots of a chloroform solution of the precipitate gave almost identical results. Agreement between replicates is seen to be very good in most instances and the results close to those of analyses by classical methods. In those cases where there is an appreciable deviation among replicates, the samples were all metals which could not be crushed, and which therefore admit the possibility of segregation and sampling errors.

A statistical analysis was made of a ferrochromium containing 72.1% chromium (BCS 203/1). An alloy with a high chromium content was chosen, as this provides a more searching test of the precision of the method. Triplicate determinations were made on ten samples; the mean of the thirty results was 72.13%, with a mean deviation of ± 0.6%. 8-Hydroxyquinaldine was used as reagent.

(c) *Analysis of ferrovanadium*

No figure is given in table (b) for the determination of chromium in ferrovanadium by standard methods as no sufficiently accurate method is known, and results were judged by comparison with synthetic mixtures. Two solutions were prepared:

A. A solution containing iron and vanadium in the same concentration as would be given by 0.2 g of a ferrovanadium containing 35% vanadium in 250 ml.

B. A solution containing 0.01734 g of chromium as potassium dichromate in one litre.

Then 5 and 10 ml portions of B were added to 25 ml portions of A and the mixture was precipitated with 8-hydroxyquinaldine. The results are given in the table below. In part (1) the dichromate was reduced by boiling with 1 ml of alcohol. In part (2) smaller volumes of B were added, and the dichromate was reduced by the 8-hydroxyquinaldine.

	B added to 25 ml of A ml	*Chromium added* mg	*Chromium found* mg
(1)	0	0	0.005
	5	0.0867	0.090
	10	0.173	0.176
(2)	0	0	0.000
	1.25	0.0217	0.022
	2.5	0.0433	0.044

Notes on reagents and instruments

(a) *Benzene, chloroform and trichloroethylene*: any reagent grade solvents may be employed, but they should be dried over calcium chloride before use. Chloroform and trichloroethylene containing hydrogen chloride or phosgene must never be used, as these impurities decompose the organic complexes. The alcohol added to the chloroform as a preservative must not be removed, and all the chloroform used in any one determination must be drawn from the same stock bottle. When aliquots are taken of the chloroform solution, the bulk of this solvent may be recovered by distillation and used again without further purification, but alcohol, up to 1% by weight, may have to be added occasionally to prevent photodecomposition. In order to ensure that no change in light transmittance at 410 or 425 mμ occurs when the mixed solvent is passed through an alumina column, a blank test should be made on the fresh and eluted solvent.

(b) 8-*Hydroxyquinoline*: it is desirable to use analytical reagent grade material, but any good laboratory reagent grade will suffice.

(c) 8-*Hydroxyquinaldine*: the commercial material is expensive and is impure. This reagent may be prepared cheaply by the method described by MERRITT AND WALKER[11], with the modification that the vacuum distillation of the steam-distilled product is omitted, resulting in an increase in yield from 5.2% to 54%, based on the amount of *o*-aminophenol hydrochloride used.

(d) *Activated alumina*: all the work described in this paper has been based on the Peter Spence product, Type H (100-200 mesh). This alumina requires no further activation before use, but must be stored in a tightly closed container. Its activity is between Brockmann Grades I and II[12].

(e) *Spectrophotometer*: The optical density measurements were made on a Unicam S.P. 600 Spectrophotometer.

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SUMMARY

A new method is described for the determination of chromium. In a suitable solution, trivalent chromium is precipitated as its 8-hydroxyquinolate, or 8-hydroxyquinaldate, in the presence of trivalent iron. The dried precipitate is dissolved in chloroform, and the solution, diluted once with benzene, is passed through an activated alumina chromatographic column. The optical density of the eluate, containing the chromium complex only, is measured at 410 or 425 mμ with respect to the solvent. Aluminium, vanadium and cobalt interfere when 8-hydroxyquinoline is used as reagent; but when 8-hydroxyquinaldine is used, the method is unequivocal.

RÉSUMÉ

Une nouvelle méthode est décrite pour le dosage du chrome. Dans certaines conditions, le chrome(III) peut être précipité sous forme de 8-hydroxyquinoléate ou de 8-hydroxyquinaldate,

en présence de fer(III). Le précipité séché est dissous dans le chloroforme; ensuite la solution, diluée une fois avec le benzène, est passée à travers une colonne chromatographique d'alumine activée. La densité optique de l'éluat, renfermant le complexe du chrome seulement, est mesurée à 410 ou 425 mμ, en comparant avec le solvant. L'aluminium, le vanadium et le cobalt gênent lorsqu'on utilise la 8-hydroxyquinoléine comme réactif, mais ils ne gènent pas lorsqu'on utilise la 8-hydroxyquinaldine.

ZUSAMMENFASSUNG

Eine neue Methode zur Bestimmung von Chrom wird beschrieben. In einer geeigneten Lösung kann das dreiwertige Chrom in Gegenwart von dreiwertigem Eisen als 8-Oxychinolat oder 8-Oxychinaldat gefällt werden. Der getrocknete Niederschlag wird in Chloroform gelöst, die erhaltene Lösung einmal mit Benzol verdünnt und an aktiviertem Aluminiumoxyd chromatographiert. Die optische Dichte des Eluates, welches nur den Chromkomplex enthält, wird bei 410 oder 425 mμ im Vergleich zum Lösungsmittel gemessen. Aluminium, Vanadin und Kobalt stören wenn 8-Oxychinolin als Reagenz verwendet wird; bei Gebrauch von 8-Oxychinaldin ist die Methode eindeutig.

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SUR LA RÉACTION COLORIMÉTRIQUE DE L'ALUMINIUM AVEC LA QUINALIZARINE

par

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Un travail de revision des principales techniques colorimétriques de l'aluminium, effectué sous les auspices de la Commission Internationale de Chimie Analytique de l'Union Internationale de Chimie Pure et Appliquée, nous a conduits à l'étude de la réaction entre l'aluminium et la quinalizarine.

PARTIE EXPÉRIMENTALE

Appareils et solutions: Pour les mesures spectrophotométriques, on utilise un spectrophotomètre Beckman modèle DU et pour les mesures de pH un appareil Beckman avec électrode de verre.

La solution étalon d'aluminium contient 112 mg d'aluminium dans 1 litre (dosé gravimétriquement), sous forme de chlorure d'aluminium; on prépare ensuite diverses solutions de concentration connue, par dilution.

Réactif: Jusqu'à présent, on employait des solutions alcooliques saturées de réactif; pour nos mesures, il nous a paru plus avantageux de préparer des solutions alcalines, permettant d'obtenir des concentrations plus grandes et constantes. On prépare les solutions de 1,2,5,8-tétrahydroxyanthraquinone en dissolvant 0.100 g dans 100 ml de NaOH 0.1N (exempt de Al). Les solutions ainsi préparées sont assez stables.

Solution tampon: On la prépare en ajoutant 10 volumes d'acide acétique 5N à 9 volumes d'ammoniaque 5N. On obtient un pH compris entre 5.4 et 5.9.

Formation du composé coloré

Selon la méthode de KOLTHOFF[1] à pH compris entre 5.4 et 5.8, l'aluminium forme une laque bleu violet avec une solution alcoolique de quinalizarine. La coloration apparaît après 15 minutes à froid ou en chauffant à 50° C.

Nous nous basons sur nos résultats expérimentaux pour apporter à la méthode précédente quelques modifications.

1) Formation du composé coloré, en employant une solution alcaline du réactif, la réaction est alors très rapide même à froid.

2) Emploi d'une solution très diluée de gélatine comme stabilisateur du composé formé, on obtient ainsi une solution transparente et stable pendant 12 heures.

3) Lorsqu'on a obtenu le composé coloré, on ajoute la solution tampon acide acétique-ammoniaque (pH de 5.9), l'excès du sel de sodium de la quinalizarine se transforme en quinalizarine libre légèrement jaune, tandis que la laque est parfaitement stable.

On a prouvé que le pH optimum pour la formation de la laque est celui que Kolthoff a fixé.

Courbes d'absorption du réactif et du composé coloré

Dans la région du spectre visible les courbes de densités optiques en fonction de la longueur d'onde du réactif et du composé coloré sont représentées sur la Fig. 1. La quinalizarine, au pH 5.8, présente un maximum d'absorption à 460 mμ, et au pH 10.5, deux maxima proches à 550 et 580 mμ. Pour le composé qui se forme entre l'aluminium et la quinalizarine on obtient un maximum d'absorption à 535 mμ. Comme on peut le voir sur les courbes de longueur d'onde au maximum d'absorption du composé coloré, la quinalizarine présente encore une absorption considérable.

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* présenté au XLVe Congrès International de Chimie Pure et Appliquée, Zurich, 1955.

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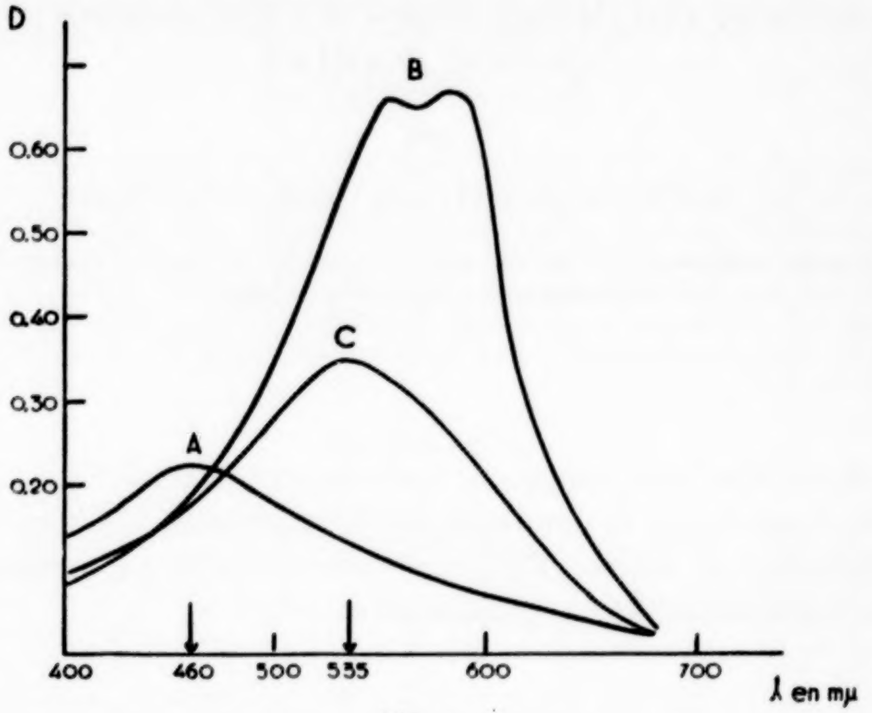

Fig. 1.

Courbe A: Spectre d'absorption de 0.3 ml de quinalizarine 0.1% dilués à 25 ml, pH = 5.8.

Courbe B: Spectre d'absorption de 0.3 ml de quinalizarine 0.1%, en solution alcaline, dilués à 25 ml, pH = 10.5.

Courbe C: Spectre d'absorption de 5 ml de sol. d'aluminium $4.14 \cdot 10^{-4} M$ et 0.3 ml de quinalizarine 0.1% dilués à 25 ml.

Etude spectrophotométrique du composé coloré

On étudie l'influence de la concentration du réactif sur l'intensité de la coloration. En prenant des quantités fixes d'aluminium et variables de quinalizarine, l'absorption augmente jusqu'à formation totale de la laque, puis se maintient constante, parallèle à la droite représentant l'absorption de la quinalizarine seule. Si on répète ces mesures pour une autre quantité constante d'aluminium on trouve le même type de courbe (Fig. 2).

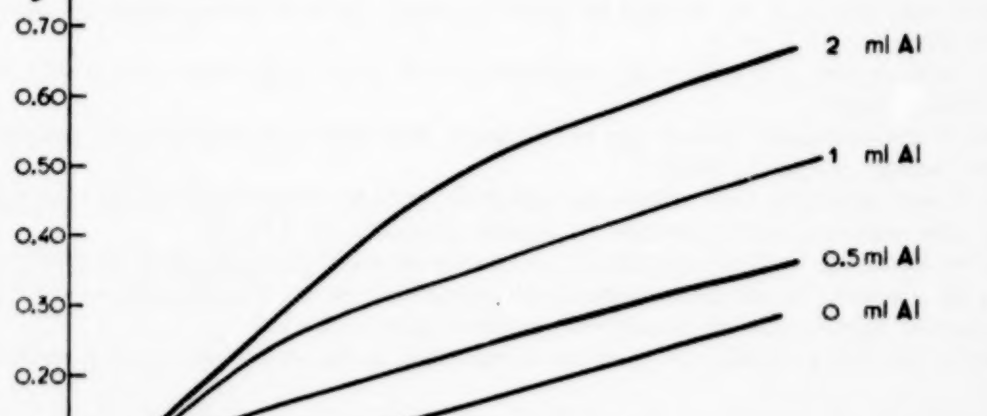

Fig. 2

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Le fait qu'un changement brusque de la pente de la courbe ne se produit pas indique que le composé est fortement dissocié en solution. Cela nous a fait supposer que l'aluminium et la quinalizarine forment un complexe de composition définie et non un composé d'adsorption comme mentionné jusqu'à présent dans la littérature. Mais le fait que ces composés se forment à des pH supérieurs aux pH de formation des hydroxydes correspondants, et que ces colorants polyhydroxyanthraquinoniques sont les plus adsorbés, appuie la théorie du composé d'adsorption. Cependant, cette adsorption du colorant sur la surface de l'oxyde hydraté peut être considérée comme un premier état qui, dans quelques cas, peut évoluer vers la formation d'un complexe interne.

La méthode de la relation molaire n'ayant pas donné des résultats sûrs, on a utilisé la méthode des variations continues proposée par JOB[2] et développée par VOSBURG ET COOPER[3] pour déterminer la proportion dans laquelle l'aluminium et la quinalizarine réagissent.

Nous représentons dans un graphique, à une longueur d'onde déterminée, les densités optiques des mélanges obtenus en fonction de x litres de réactif et nous obtenons une courbe qui passe par un maximum. Comme l'extinction molaire du réactif à la longueur d'onde employée (535 mμ) n'est pas nulle nous obtenons une seconde courbe pour les densités optiques de la quinalizarine seule (voir Fig. 3).

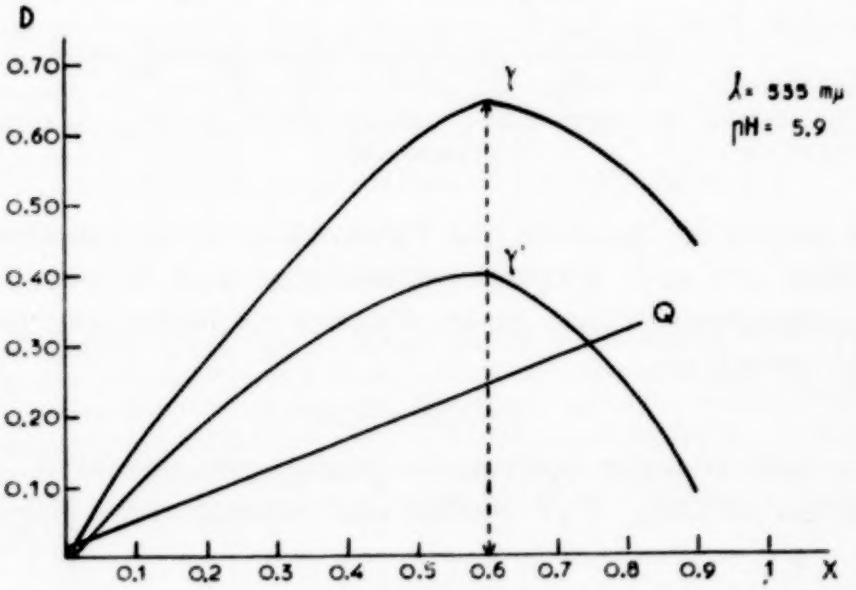

Fig. 3. x litres de solution de réactif $4.14 \cdot 10^{-4} M$ ajoutés à $1-x$ litres de solution d'aluminium $4.14 \cdot 10^{-4} M$.

La valeur de x dans laquelle la fonction y passe par un maximum nous donnera la valeur de n dans la formule du complexe Al(Quin.)$_n$ selon la relation $n = \frac{x}{1-x}$. Dans la Fig. 3 on peut observer que le maximum se trouve à 0.60 et par conséquent n sera 1.50.

Cette position du maximum se maintient lorsqu'on augmente les concentrations molaires des solutions d'aluminium et de quinalizarine, comme on peut le voir dans la Fig. 4.

En changeant légèrement les longueurs d'onde auxquelles on effectue les mesures, le maximum de la courbe correspond toujours à la relation molaire obtenue ci-dessus, ce qui démontre qu'il ne se forme qu'un seul composé (Fig. 5).

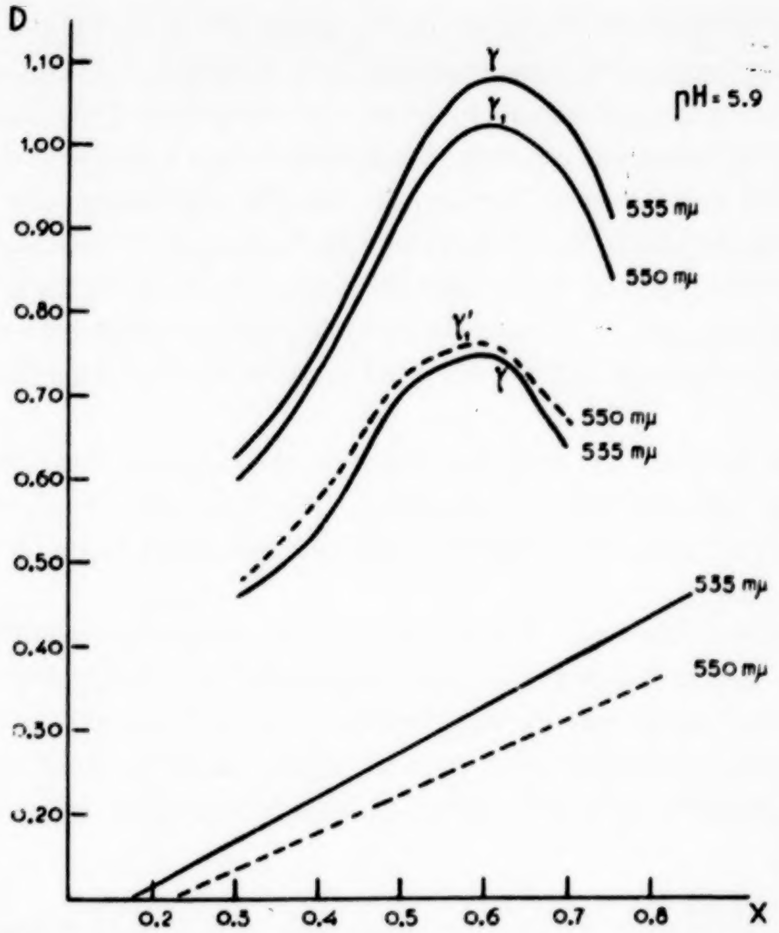

Fig. 4. *x* litres de solution de réactif $8.28 \cdot 10^{-4} M$ ajoutés à 1-*x* litres de solution d'aluminium $8.28 \cdot 10^{-4} M$.

Ceci nous a permis de supposer que l'aluminium et la quinalizarine réagissent dans la proportion 2:3 et le composé qui se forme aura la formule $Al_2(C_{14}H_8O_6)_3$. Il faudrait évidemment utiliser encore d'autres méthodes pour pouvoir établir la structure de ce complexe.

CONCLUSIONS

Cette étude a prouvé qu'on obtient une plus grande sensibilité en employant le réactif en solution alcaline, il en résulte une concentration définie et constante.

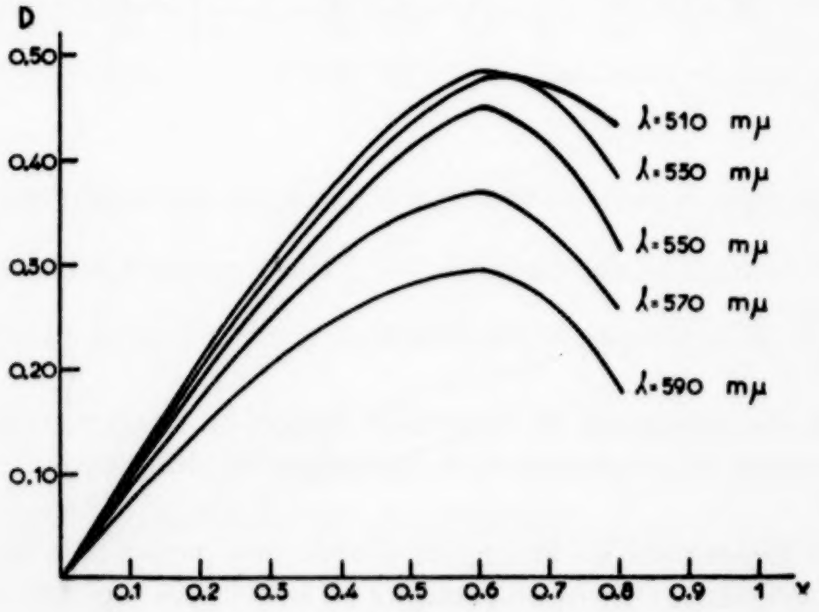

Fig. 5

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On obtient également une plus grande stabilité du composé formé en utilisant de la gélatine pour faciliter la dispersion colloïdale.

Le spectre d'absorption de la quinalizarine, à pH 4.9, présente un maximum à 460 mμ, tandis que dans un milieu alcalin, à pH 10.5, il y a deux maximums à 550 mμ et 580 mμ. Le complexe aluminium-quinalizarine présente un maximum à 535 mμ.

L'application de la méthode des variations continues nous a permis d'arriver à la conclusion qu'il se forme un composé dans la proportion 2:3.

La quinalizarine présente relativement peu d'intérêt pour le dosage de l'aluminium; il existe d'autres méthodes beaucoup plus avantageuses.

RÉSUMÉ

Nous avons étudié la réaction colorimétrique entre l'aluminium et la quinalizarine et, comme conclusion de nos observations, nous apportons quelques modifications dans les méthodes analytiques utilisées jusqu'à présent.

Nous avons étudié les courbes d'absorption du composé coloré et de la quinalizarine à différents pH. Nous appliquons la méthode des variations continues pour déterminer la composition du produit de réaction. De ces mesures spectrophotométriques, on peut déduire que les constituants forment un composé défini dans la proportion 2:3.

SUMMARY

The reaction between aluminium and quinalizarin has been studied, and some modifications have been made to the analytical procedure usually followed.

The absorption curve of the Al-quinalizarin compound and that of quinalizarin alone have been drawn. We applied the continuous variations method in order to determine the structure and composition of the reaction product. The spectrophotometric readings have shown that the constituents of the coloured compound are bound in a definite ratio, 2:3.

ZUSAMMENFASSUNG

Auf Grund einer Untersuchung der Reaktion zwischen Aluminium und Chinalizarin wurden einige Änderungen der üblichen analytischen Methoden vorgeschlagen.

Die Absorptionskurven von Chinalizarin und der gefärbten Al-Chinalizarin-Verbindung wurden aufgezeichnet. Um die Zusammensetzung der Al-Chinalizarin-Verbindung zu ermitteln, wurde die Methode der „kontinuierlichen Variationen" angewendet. Aus den Ergebnissen der photometrischen Messungen wurde geschlossen, dass die gefärbte Verbindung die Komponenten im Verhältnis 2:3 enthält.

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A PRECISE DIRECT HETEROMETRIC DETERMINATION OF TRACES OF COPPER WITH DIETHYLDITHIOCARBAMATE IN EXCESSES OF METALS

by

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INTRODUCTION

The determination of traces of copper with diethyldithiocarbamate (= CBM) has been studied extensively in recent years and there are numerous publications on this subject[1]. These studies were mostly concerned with the determination of copper in water, milk, other food stuffs and biological materials. Special attention was given to the determination of copper in excess of ferric iron. It was the purpose of the investigation to find the necessary conditions for a precise heterometric determination of copper with CBM. In previous investigations the reaction between mercury and CBM was studied by the authors[2]. As the material presented in this paper shows, the heterometric determination could be carried out very successfully in the suitable milieu with the presence of complexing agents. The reaction concerned is approximately of the same sensitivity as the reaction between cobalt and α-nitroso β-naphthol; 0.1–0.3 mg copper in 20 ml solution can be determined. Working conditions are presented which enable the heterometric determination of copper to be carried out in 7–10 minutes. The precision achieved was so great that in almost all cases theoretical values for copper were obtained without dependence on the amount of copper present. Generally, the copper made up only 0.1–0.2% of the total metal content. The determination of 0.06% of copper in iron presented no difficulties whatsoever. Compared with the heterometric titration of cobalt with α-nitroso β-naphthol[3] the reactions between copper and CBM required only *one third* of the time for a complete titration.

All the above advantages place the presented method in a position of primary importance and make its application universal for the direct heterometric determination of copper in metals, etc.

EXPERIMENTAL

Apparatus. A "Heterometer", designed by the first author, was used[4]. The light passed vertically through a cylindrical absorption cell of 4 cm diameter (in the experiments described in this paper) onto the photoelectric cell. The readings on the galvanometer were made with an accuracy of ± 0.001 microampere. They were recorded after increments of 0.1-0.2 ml of titrant were added, only when a constant value had been obtained, usually after a few seconds. The constancy of stirring of the solution was electronically controlled. The titrant was added from a 5 ml microburette (0.01 ml) the tip of which was dipped in the solution being analysed.

Temperature. All heterometric titrations were thermostatically controlled and were carried out at 20° C. A controlled temperature is generally unnecessary as the accuracy of the determination is independent of the temperature in the limits of ordinary room temperatures. Only the absolute *values* of the optical density are influenced by the temperature; these are more constant and more easily controlled when experiments, carried out at different times and at a constant temperature, are compared.

Stirring. The rate of stirring of the solution was generally the maximum consistent with stable measurements.

Readings. Readings of the galvanometer were constant in a few seconds in the presence of the supplementary neutral electrolyte (NH_4NO_3). This was just as fast as in a regular homogeneous titration.

Reproducibility. On repeating titrations at different times it was found that the maximum optical density values obtained did not change by more than one unit in the second decimal place.

Volume. The volume analysed was, in all cases, 20 ml (aqueous solution), containing 0.19 mg-0.254 mg of copper. The molarity of the copper in the analysed solution was, therefore, $5 \cdot 10^{-5}$-$6.7 \cdot 10^{-5} M$ or 1 part copper per 100,000 parts of solution.

Reagent. The sodium diethyldithiocarbamate (= CBM) was an Eastman Kodak reagent. Diluted CBM solutions were often prepared from a stock solution which was stored in a dark brown bottle. The stock solution was stable for months. All other chemicals used, were either analytical reagents or chemically pure reagents.

RESULTS

General aspects

Accuracy. Almost all of the titrations presented were carried out with the highest accuracy and the determinations of copper were made with an error equal to zero. In spite of this a titration lasted only 7-10 minutes.

In the following tables and figures a selection of results obtained in the heterometric study of the reaction between copper and carbamate (= CBM), are presented. The numeration is the same in the tables and in the figures. The copper can be precipitated from acidic, neutral or alkaline solutions and the pH of the solution is probably not of primary importance. The presence of neutral electrolytes in a sufficient concentration is of greater importance for the heterometric titration. This factor determines whether precipitation occurs at all, and whether the precipitate can be used, for a quick an precise determination of copper. A further problem is the kind of complexing agents and their concentration which could be used without interfering with the heterometric precipitation of copper.

Table I and Fig. 1 present some results obtained in the *absence* of foreign metals on changing the composition and the concentration of the electrolytes in the solution. As was ascertained the *ammoniacal citrate solution was the most favorable for the heterometric titrations.* In the presence of *ammonium nitrate* the titration proceeded very quickly, and the *first* maximum optical density point was determined easily and with precision. *In the presence of citrate a horizontal maximum line* was obtained immediately after the first maximum point. In the absence of citrate the densities generally dropped after the first maximum. From previous studies[5] on the composition and the structure of citrate complexes we know that these are mostly stable in the alkaline solution. No other complexing agents could compete with citrate in these heterometric titrations. A large number of experiments were carried out by us with *ethylenediaminetetraacetate* (= EDTA) in an alkaline medium both in the presence and in the absence of excesses of foreign metals. Although the end-point of the titration could be fixed in many cases, the results were not sufficiently sure, smooth curves were not obtained and the titration generally lasted a longer time.

TABLE I

Composition: 3 ml *a M* $Cu(NO_3)_2$ + *K* ml supplements + (17-*K*) ml H_2O + *x* ml 0.0028*M* CBM. T = 20° C. Content Cu 0.190 mg, 0.254 mg, 0.381 mg.

Expt. number	Molarity of $Cu(NO_3)_2$ (a)	Supplements	Found					
			ml CBM (x)	Maximum density value	Initial prepn. ml	Titration time (min)	Theoretical point ml	Error %
1	0.00133	2 ml 2*M* NH_3	3.00	0.51**	0.1	45	3.00	0.0
2	0.00133	4 ,, *M* CH_3COONa		0.29****		20		
3	0.00133	2 ,, 2*M* NH_3 + 4 ml *M* NH_4NO_3	3.00	0.57**	0.1	10	3.00	0.0
4	0.002	2 ,, 2*M* ,, + 2 ,, ,, ,,	4.54	0.77	0.1	15	4.5	0.9
5	0.001	2 ,, 2*M* ,, + 2 ,, ,, ,,	2.20	0.50**	0.1	15	2.25	−2.2
6	0.002	2 ,, 2*M* ,, + 5 ,, ,, ,,	4.50	1.00	0.1	10	4.5	0.0
7	0.001	2 ,, 2*M* ,, + 5 ,, ,, ,,	2.25	0.34**	0.1	20	2.25	0.0
8	0.001	2 ,, 2*M* ,, + 2 ,, ,, ,, + 3 ml *M* Na_3-citrate	2.30	0.45**	0.1	20	2.25	2.2
9	0.00133	2 ,, 2*M* ,, + 4 ,, ,, ,, + 3 ,, ,, ,,	3.00	0.51*	0.1	10	3.00	0.0
10	0.00133	1 ,, conc. ,, + 4 ,, ,, ,, + 3 ,, ,, ,,	3.00	0.48*	0.1	10	3.00	0.0
11	0.002	2 ,, 2*M* ,, + 4 ,, ,, ,, + 3 ,, ,, ,,	4.50	0.60*	0.1	8	4.50	0.0
12	0.00133	1 ,, conc. — + 9 ,, ,, ,,	3.00	0.40*	0.1	10	3.00	0.0
13	0.00133	2 ,, 2*M* ,, + 4 ml *M* NH_4NO_3 + 5 ,, ,, ,,	3.00	0.35*	0.1	10	3.00	0.0
14	0.001	2 ,, 2 ,, ,, + 5 ,, ,, ,, + 3 ,, ,, ,,	2.33	0.45**	0.1	10	2.25	3.5
15	0.00133	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, K_2-tartrate	3.00	0.48	0.1	10	3.00	0.0
16	0.001	1 ,, conc. ,, + 4 ,, ,, ,, + 3 ,, ,, ,,	2.27	0.51**	0.1	10	2.25	0.9
17	0.001	2 ,, 2*M* ,, + 5 ,, ,, ,, + 8 ,, 0.125*M* $Na_4P_2O_7$	2.30	0.44**	0.1	15	2.25	2.2
18	0.00133	1 ,, conc. ,, + 4 ,, ,, ,, + 11 ,, 0.125*M* ,,	3.00	0.44*	0.1	10	3.00	0.0
19	0.00133	1 ,, ,, ,, + 4 ,, ,, ,, + 10 ,, 0.2*M* Na_4-EDTA	3.00	0.58***	1.6	20	3.00	0.0
19a	0.00133	2 ,, 2*M* ,, + 4 ,, ,, ,, + 5 ,, 0.1*M* ,,	3.00	0.62***	0.1	22	3.00	0.0

CBM = Sodium diethyldithiocarbamate; EDTA = Ethylenediaminetetraacetate;

* after the maximum a horizontal density line;
** after the maximum density decreases;
*** no smooth titration curve;
**** fluctuation.

TABLE II

Composition: 3 ml 0.0013M $Cu(NO_3)_2$ + K ml supplements + (17-K) ml H_2O + x ml 0 0028M CBM. T = 20° C. Content Cu 0.254 mg (0.38 mg).

Expt. number	Supplements	Cu %	Found ml CBM (x)	Found Maximum density value **	Found Error %
20	2 ml 2M NH_3 + 4 ml M NH_4NO_3 + 2 ml M $Ca(NO_3)_2$	0.31	3.00	0.51	0.0
21	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 2 ,, ,, $SrCl_2$	0.14	,,	0.52	,,
22	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 2 ,, ,, $BaCl_2$	0.09	,,	0.50	,,
23	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 2 ,, ,, $MgCl_2$	0.52	,,	0.48	,,
24	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 11 ,, 2M ,,	0.04	,,	0.35	,,
25	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, M Na_3-citrate + 2 ml M $Zn(NO_3)_2$	0.19	,,	0.42	,,
26	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 2 ,, ,, $NiCl_2$	0.21	,,	0.39	,,
27	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 2 ,, ,, $CoCl_2$	0.21	,,	0.25	,,
*28	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 2 ,, ,, ,,	0.32	4.50	0.35	,,
29	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 2 ,, ,, $MnCl_2$		∞	0.7	,,
30	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 2 ,, ,, $CdCl_2$	0.10	3.00	0.44	,,
31	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 2 ,, ,, $Pb(NO_3)_2$	0.06	,,	0.58	,,
32	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 8 ,, 0.1M $TlNO_3$	0.15	,,	0.69	,,
33	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 10 ,, 0.1M $AgNO_3$		∞	0.0	,,
34	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 2 ,, M $AlCl_3$	0.46	3.00	0.55	,,
35	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 5 ,, ,, ,, + 4 ,, ,, ,,	0.23	,,	0.33	,,
36	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 2 ,, 0.1M $Cr(NO_3)_3$	2.4	,,	0.50	,,
37	1 ,, conc. ,, + 4 ,, ,, ,, + 5 ,, ,, ,, + 4 ,, M $FeCl_3$	0.11	,,	0.45	,,
38	1 ,, ,, ,, — + 9 ,, ,, ,, + 6 ,, M ,,	0.075	,,	0.33	,,
39	1 ,, ,, ,, + 4 ml M NH_4NO_3 + 3 ,, ,, ,, + 2 ,, 0.1M $SbCl_3$	1.03	,,	0.48	,,
40	2 ,, 2M ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 5 ,, 0.1 ,, $Ce(NO_3)_3$	0.36	,,	0.50	,,
41	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 8 ,, 0.1 ,, $La(NO_3)_3$	0.23	,,	0.54	,,
42	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 2 ,, M $ZrO(NO_3)_2$	0.17	,,	0.48	,,
43	2 ,, 2 ,, ,, + 4 ,, ,, ,, — + 1 ,, ,, Na_2MoO_4	0.26	,,	0.64	,,
44	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, M Na_3-citrate + 2 ,, 0.1M $Th(NO_3)_4$	0.54	,,	0.64	,,

CBM = Sodium diethyldithiocarbamate; initial precipitation throughout at 0.1 ml CBM; titration time 7-10 minutes;

* 3 ml 0.002M $Cu(NO_3)_2$;
** horizontal maximum line in all experiments;
∞ no end-point.

Tartrate in alkaline solution could in no way compete with the citrate: in the former case a precipitate usually appeared in the presence of foreign metals *before* the carbamate was added. Titrations with carbamate could only be carried out when the concentration of the foreign metal was low.

In spite of this there are many special cases in which tartrate could be used more successfully than citrate (*e.g.* Sb).

The use of *pyrophosphate* evidently gave no better results. Furthermore, the solubility of sodium pyrophosphate is many times lower than that of trisodiumcitrate or tartrate.

Table II and Figs. 2 and 3 present results obtained in the presence of excesses of foreign metals in alkaline citrate solutions. Table III and Fig. 4 likewise show these results in the presence of tartrate.

The results presented in this work are of interest for many reasons. Firstly, the amount of the foreign metals which may be present in solution, without any influence on the titration of copper, is very high. This concerns metals which could not be satisfactorily detected by direct methods or for the detection of which no direct methods exist. Secondly, the copper could be determined in almost all cases *with an error which is equal to zero*. In spite of this, the heterometric titrations of copper with carbamate required no more

TABLE III

Composition: 3 ml *a* *M* $Cu(NO_3)_2$ + 4 ml *M* NH_4NO_3 + 3 ml *M* K_2-tartrate + *K* ml supplements + (10-*K*) ml H_2O + *x* ml *b* *M* CBM. T = 20° C.
Content Cu 0.254 mg, 0.127 mg.

Expt. number	*Molarity of*		*Supplements*	*Cu* %	*Found*			*Error* %
	$Cu(NO_3)_2$ (a)	*CBM (b)*			*ml CBM (x)*	*Maximum density value*	*Titration time min*	
45	0.00133	0.0028	2 ml 2*M* NH_3 + 2 ml *M* $AlCl_3$	0.46	3.00	$0.52^{1)}$	10	0.0
46	0.00133	0.0028	1 ,, conc. ,, + 6 ,, 0.1*M* $SbCl_3$	0.35	3.00	$0.62^{1)}$	10	,,
47	0.00133	0.0028	1 ,, ,, ,, + 9 ,, 0.1 ,, ,,	0.23	3.00	$0.88^{1)}$	10	,,
48	0.00066	0.0014	1 ,, ,, ,, + 9 ,, 0.1 ,, ,,	0.11	3.00	$0.40^{2)}$	15	,,
49	0.00133	0.0028	2 ,, 2*M* ,, + 8 ,, 0.1 ,, $Th(NO_3)_4$	0.13	3.00	$0.65^{1)}$	10	,,
50	0.00133	0.0028	2 ,, 2 ,, ,, + 8 ,, 0.1 ,, $VOSO_4$	0.61	3.00	$0.55^{1)}$	10	,,
51	0.00133	0.0028	2 ,, 2 ,, ,, + 8 ,, 0.1 ,, Na_2MoO_4	0.33	3.00	$0.60^{2)}$	10	,,
52	0.00133	0.0028	2 ,, 2 ,, ,, + 4 ,, 0.2 ,, $ZrO(NO_3)_2$	0.35	3.00	$0.44^{1)}$	10	,,
53	0.00133	0.0028	1 ,, conc. NH_3 + 8 ,, *M* K_2-tartrate + 6ml *M* $AlCl_3$	0.16	3.00	$0.35^{1)}$	9	,,

CBM = Sodium diethyldithiocarbamate; 1) after the maximum a horizontal density line;
2) after the maximum, the density decreases. Initial precipitation always at 0.1 ml CBM.

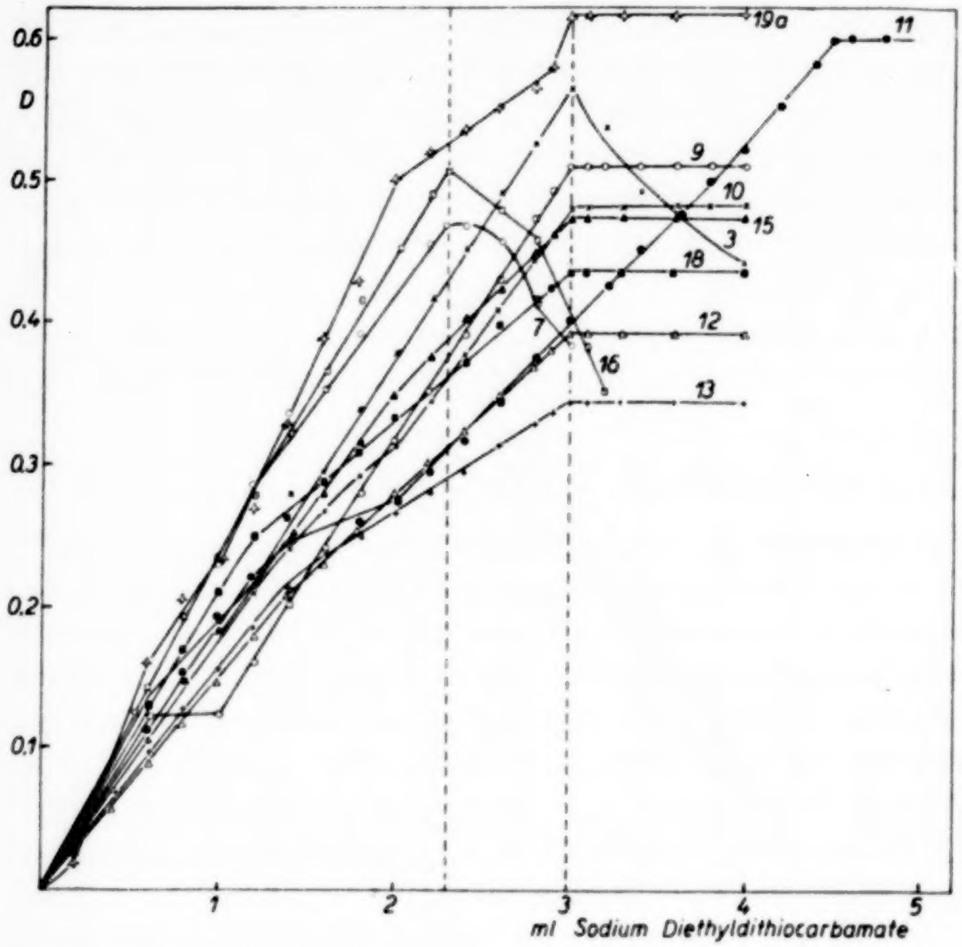

Fig. 1. Titrations of copper in the presence of complexing agents.

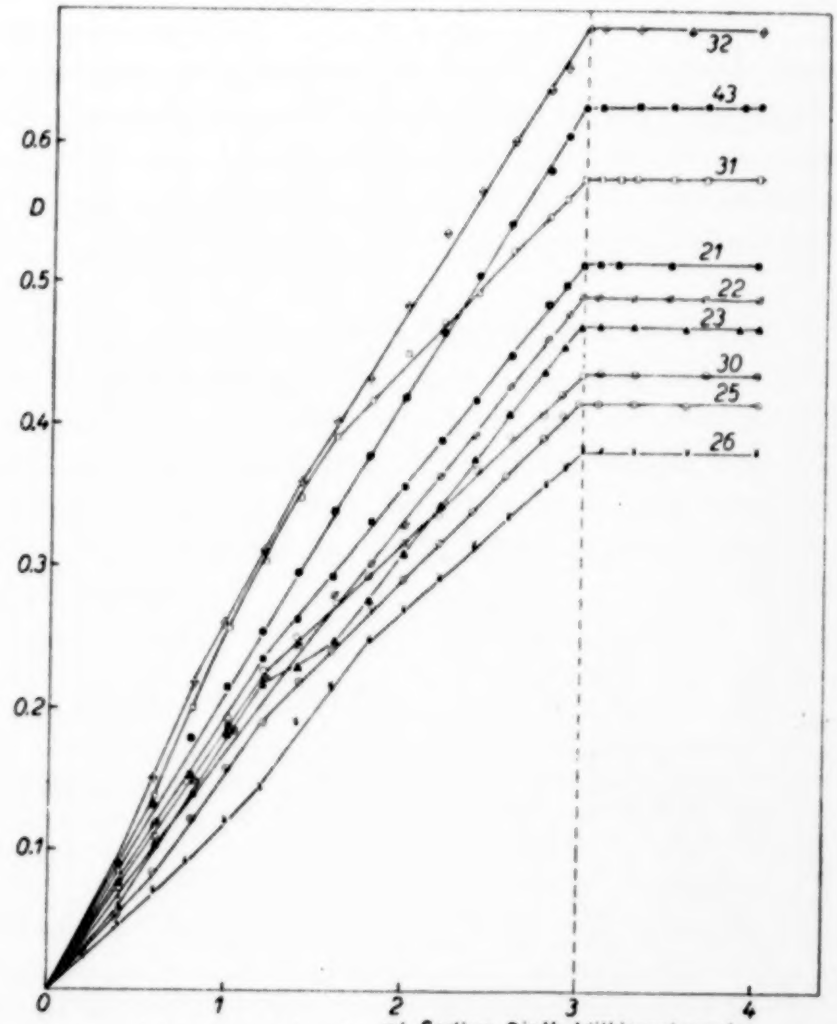

Fig. 2. Titrations of copper in citrate solution in the presence of excesses of foreign metals.

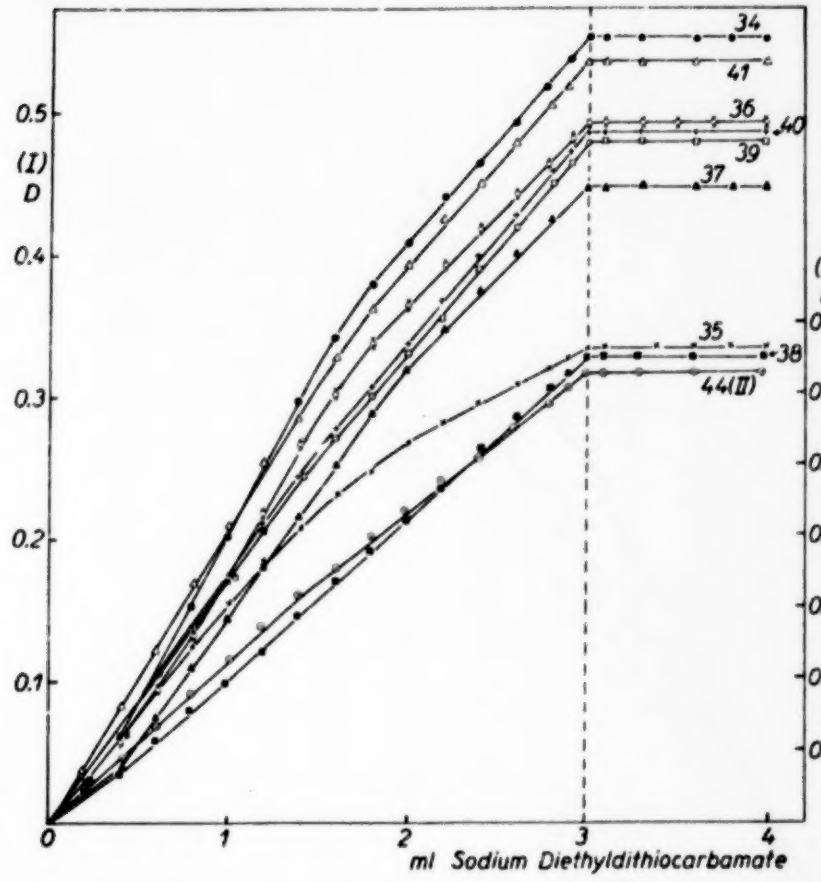

Fig. 3. Titrations of copper in citrate solution in the presence of excesses of polyvalent cations.

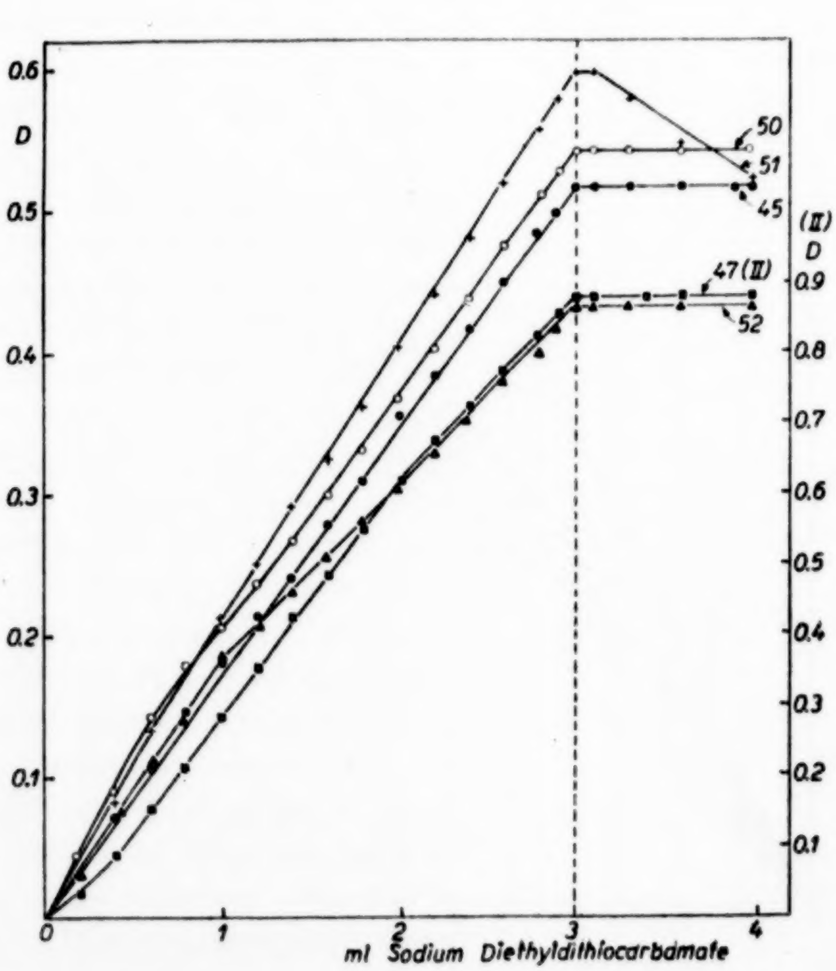

Fig. 4. Titrations of copper in tartrate solution in the presence of excesses of foreign metals.

than 7 to 10 minutes. The following calculation demonstrates the sensitivity and the precision of the direct heterometric determination of traces of copper with CBM in the presence of $\gtrsim$ 99.8% other metals.

In analysing 0.2 mg copper in 20 ml solution, 1 part of copper in 100,000 parts of solution is determined. Since the titrant is added in increments of 0.1 ml and the copper is determined with a zero error (using 3 ml CBM for a full titration) an amount of copper which is 30 times less than that contained in the analysed solution can be safely determined. This means that 1 part of copper in 3,000,000 parts of solution can be determined with an error equal to zero.

Titrations in the presence of neutral supplements and complexing agents

In the presence of *sodium acetate* (expt. 2) the titration was unsafe because the readings fluctuated. A satisfactory end-point could not be obtained. When the titration was carried out in the presence of an *excess of ammonia* but in the *absence* of ammonium nitrate (expt. 1) the titration lasted about *five times* as long as in the presence of the latter. Apart from this, the maximum density values and the precision were the same in both cases. It is likely that the favorable action of *ammonium nitrate* was caused by its presence as a concentrated neutral electrolyte. A sufficient amount of ammonium nitrate was therefore added to all solutions to be analysed. In the very *dilute* solutions of copper, excesses of ammonium nitrate seemed to decrease the maximum density value somewhat (expts. 5 and 7). Even in the presence of sodium citrate no horizontal maximum density line was obtained and the density values dropped after the maximum point.

In general the addition of excesses of *trisodium citrate* to the analysed copper solutions was favorable for the titration. Smooth titration curves were obtained in all cases. The precise location of the *first* maximum density point was very simple because a *horizontal density line* was obtained immediately after the first maximum point (expts. 9-13). If, however, too great an excess of titrant was added the density values began to decrease again.

To a certain extent, tartrate, pyrophosphate, tripolyphosphate and ethylenediaminetetraacetate (= EDTA) could be used as complexing agents (expts. 15 and 18). In the presence of EDTA in ammoniacal solution the end-point of the titration was located but the curves were not smooth and the titration time was longer than usual (expts. 19 and 19a). Summarizing, it may be said that *the titration of copper proceeded quickly and safely when an ammoniacal solution was used, containing excesses both of ammonium nitrate and of sodium citrate.*

Titrations in the presence of excesses of foreign metals

In the presence of Ca, Sr, Ba and Mg. No complexing agents whatever were necessary (expts. 20-23). The influence on the maximum density value of the blank was not appreciable. Probably the salts could have been present in much higher concentrations. In all cases the percentage of copper was 0.15-0.3%. At the higher concentration of magnesium the maximum value decreased (expt. 24) and in this case the use of a somewhat higher amount of copper would have been preferable.

In the presence of Zn^{+2} and Cd^{+2}. The determination was carried out most successfully with trisodium citrate in a mole per mole amount at least equal to the foreign metal (expts. 25 and 30). Probably the concentration of the foreign metals could have been higher than that used. The copper made up 0.1-0.2% of the total metal content. Tartrate was also used as a complexing

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agent, but because of the insolubility of the tartrates the content of the foreign metal had to be lower.

In the presence of Mn^{+2}. In the presence of ammoniacal citrate, the density rose continuously after the calculated end-point had been reached (expt. 29). The same experiment, when carried out in an excess of ammoniacal ethylenediaminetetraacetate, (= EDTA) gave a clear end-point at the calculated point but no smooth titration curve was obtained.

In the presence of Co^{+2} and Ni^{+2}. Sodium citrate was used as complexing agent, (expts. 26-28). The copper made up 0.2-0.3% of the total metal content. The maximum density value was considerably lower in the presence of cobalt.

In the presence of Pb^{+2}. The citrate solution must be strongly ammoniacal and an excess of citrate must be present (the soluble complexes of lead citrate are discussed elsewhere[6]). The copper amounted to 0.06% of the total metal content (expt. 31). The maximum density obtained was high.

In the presence of Al^{+3}. The determination was carried out either in ammoniacal citrate or tartrate solutions. In both cases a molar excess of the complexing agent, calculated on the amount of aluminium present, must be added (expts. 34, 35, 45 and 53). In expt. 53, in the presence of excesses of tartrate, the copper content was as low as 0.16%.

In the presence of Cr^{+3}. In the presence of citrate the amount of chromium had to be very low, otherwise precipitation occurred before the addition of titrant. More chromium was present in tartrate solution. The densities in the latter cases were very low. In the citrate solution the copper amounted to 2.4% (expt. 36).

In the presence of Fe^{+3}. A highly concentrated ammoniacal solution was used (expts. 37 and 38). The determination was best made in excesses of citrate. The copper amounted to 0.075%. Theoretical results were always obtained, but in the presence of a highly concentrated citrate solution the maximum density value was depressed. In excesses of tartrate, the amount of iron which could be present in solution was less than with citrate.

In the presence of Tl^{+}. The maximum concentration of Tl^{+} in the citrate solutions was less than 0.05*M* (expt. 32). The maximum density value obtained was very high (expt. 32). With tartrate, a precipitate was obtained before titrant was added.

In the presence of Ag^{+}. Neither in citrate or tartrate nor in EDTA solutions did copper precipitate when the solution contained silver (expt. 33).

In excesses of Sb^{+3}. The amount of Sb^{+3} which could be in the ammoniacal citrate solution was very low ($\leq$0.01*M*). When not low, precipitation occurred before the titration (expt. 39). In this case, the copper amounted to 1%. In contrast to this the tartrate solution contained *five* times more antimony (expts. 46-48) and the copper content was reduced to 0.23%. In expt. 48 the copper content was only 0.11%. It was interesting that in the presence of antimony the maximum density values of the copper carbamate were very high. This was evaluated in expt. 48 in which only 0.127 mg copper was used for the analysis.

In the presence of Ce^{+3} and La^{+3}. The amounts given in the table for these metals (expts. 40 and 41) are the highest that may be present in the citrate solution. The copper made up 0.2-0.4% of the metal content. The tartrates were insoluble and could not be titrated.

In the presence of ZrO^{+2}. In experiments 42 and 52 the highest amount of zirconium which could be held in the solution was used and the concentration was 0.05*M*. In the citrate solution the concentration of zirconium was equal to 0.1*M* and the copper made up 0.17% of the metal content. In the tartrate solution the zirconium was 0.05*M* and the copper amounted to 0.35%.

In the presence of Na_2MoO_4. The molybdate was at a molarity of 0.05*M* and the copper made up 0.26% (expt. 43).

In the presence of Th^{+4}. In the experiments 44 and 49 the highest amounts of Th^{+4} which could be held in solution were used. In the tartrate solution the copper content was reduced to 0.13%. The molarity of thorium nitrate was 0.01*M* (citrate) and 0.04 (tartrate).

ANALYSIS

General method: 20 ml of an aqueous solution (the composition of which is given below), containing 0.25-0.5 mg of copper, are titrated heterometrically with an aqueous solution of 0.0028*M* sodium diethyldithiocarbamate. The solution to be analysed may contain up to >99.5% of any foreign metal.

Titration time: 7-10 minutes. Error: mostly zero.

Composition: In addition to the metals, the solution to be analysed must contain the following supplements which are added in this order:

3 ml *M* Na_3-citrate + 2 ml 2*M* NH_4NO_3 + 0.5-1.0 ml conc. NH_3.

Remarks: If traces of copper have to be analysed in alloys, the molar amount of citrate (or tartrate) must exceed the molar amount of the sum of the other metals. If the copper content of aluminium is analysed, the use of potassium tartrate instead of citrate is preferable. The same is true of solutions which contain large excesses of antimony or thorium.

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SUMMARY

The most favorable conditions for the heterometric titration of copper with sodium diethyldithiocarbamate and the influence of complexing agents on the titration were investigated.

Titrations of copper were carried out in the presence of large excesses ($> 99.5\%$) of most of the common cations. A method is presented for a precise determination of traces of copper in metals and salts.

The titration time was 7-10 minutes. In most titrations the amount of copper present was determined with an error close to zero.

RÉSUMÉ

Les auteurs ont étudié les conditions de dosage hétérométrique du cuivre avec le diéthyldithiocarbamate de sodium, ainsi que l'influence de réactifs complexants. Les titrages ont été effectués en présence de la plupart des cations ordinaires en excès ($> 99.5\%$). Une méthode précise est proposée pour le dosage des traces de cuivre dans divers métaux et sels. La détermination s'effectue en 7 à 10 minutes. Des résultats théoriques ont été obtenus dans la plupart des dosages.

ZUSAMMENFASSUNG

Die Bedingungen, welche für die heterometrische Titration von Kupfer mit Natriumdiäthyldithiocarbamat am günstigsten sind, sowie der Einfluss der komplexbildenden Körper auf die Titration wurden untersucht. Titrationen von Kupfer in Gegenwart grosser Überschüsse der meisten üblichen Kationen ($> 99.5\%$) wurden ausgeführt. Eine Methode zur genauen Bestimmung von Spuren von Kupfer in Metallen und Salzen wurde vorgeschlagen. Die Titrationsdauer betrug 7-10 Minuten. Die meisten Titrationen ergaben theoretische Werte.

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POTENTIOMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS

XXI. REDUCTION WITH FERROUS ETHYLENEDIAMINE SULPHATE

CERIC SULPHATE METHOD

by

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SINGH *et al.*[1] used ferrous ethylenediamine sulphate for the indirect volumetric determinations of potassium chlorate, potassium bromate, potassium metaperiodate, potassium dichromate, potassium ferricyanide, potassium permanganate, potassium persulphate, hydrogen peroxide and ceric sulphate. The excess of ferrous ethylenediamine sulphate added to each of the substances was titrated with standard potassium permanganate, standard potassium dichromate and standard ceric sulphate solution.

SINGH *et al.*[2] also used ferrous ethylenediamine sulphate to estimate indirectly potassium permanganate, ceric sulphate, potassium chlorate, hydrogen peroxide, potassium persulphate, potassium dichromate, and potassium bromate by a potentiometric method using standard potassium permanganate as the titrant. In the present investigation these substances have been determined indirectly using ferrous ethylenediamine sulphate solution as reducing agent. The excess of standard ferrous ethylenediamine sulphate solution added to each of the substances in acid medium was titrated potentiometrically with standard ceric sulphate solution.

EXPERIMENTAL

A known weight of each substance was mixed with an excess of standard ferrous ethylenediamine sulphate solution and the mixture acidified with sulphuric acid to keep its normality between 1 to $2N$. In the case of potassium chlorate and potassium bromate the normality of the mixture with respect to the acid was kept between 4 and $6N$. The mixture containing potassium chlorate was heated to 80° C for about ten minutes in an atmosphere of carbon dioxide and then allowed to cool. In each case the excess ferrous ethylenediamine sulphate solution was titrated at 20° C against standard ceric sulphate solution by a potentiometric method. The mixture was kept stirred by a mechanical stirrer during the titrations. A bright platinum foil immersed in the solution to be titrated was used as an oxidation-reduction electrode, and this was coupled with a saturated calomel electrode through an agar-agar potassium chloride bridge. During the titration the progress of the reaction was studied potentiometrically. At the equivalence point a sharp jump in potential was observed in each titration.

A series of potentiometric titrations were performed with different amounts of each substance. One titration, as typical of the set, is recorded in Table I.

All chemicals, except ceric sulphate, used in this investigation were of guaranteed purity. Ceric sulphate was standardized with pure arsenious oxide[3].

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TABLE I

TITRATION OF 0.0221 g OF POTASSIUM PERMANGANATE MIXED WITH 25 ml OF WATER, 28.00 ml OF 0.05N FERROUS ETHYLENEDIAMINE SULPHATE AND 30 ml OF 4N H_2SO_4 AGAINST 0.05N CERIC SULPHATE SOLUTION

Ceric sulphate ml	*E.M.F. volts*	*E/C mV/ml*
0.00	0.2735	
		2
2.00	0.2780	
		2
5.00	0.2850	
		3
7.00	0.2905	
		3
9.00	0.2965	
		4
10.00	0.3000	
		4
11.00	0.3044	
		6
12.00	0.3099	
		8
13.00	0.3181	
		10
13.30	0.3211	
		12
13.50	0.3234	
		37
13.80	0.3344	
		230
14.00	0.3805	
		1354 (Maximum)
14.05	0.4482	
		1200
14.10	0.5082	
		591
14.20	0.5673	
		164
14.50	0.6166	
		67
15.00	0.6502	
		20
16.00	0.6698	
		9
17.00	0.6789	
		6
18.00	0.6851	
		5
19.00	0.6905	
		4
21.00	0.6989	
		3
23.00	0.7045	
		3
25.00	0.7104	
		2
28.00	0.7171	

The titrations, one for each substance, are represented by the curves, A to G, given in Fig. 1.

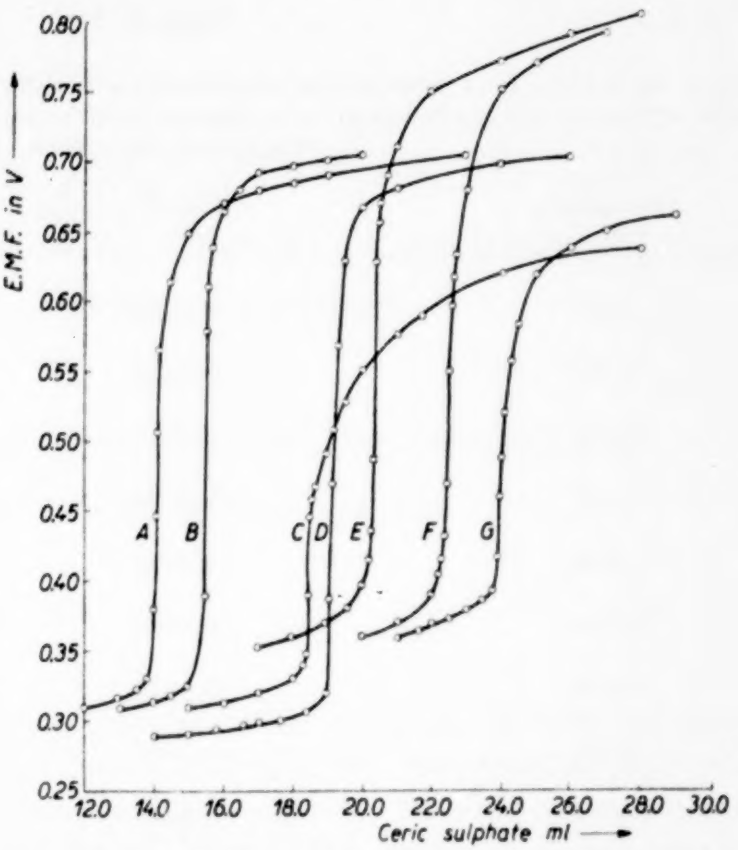

Fig. 1. Curves A $KMnO_4$
B $Ce(SO_4)_2$
C $KClO_3$
D H_2O_2
E $K_2S_2O_8$
F $K_2Cr_2O_7$
G $KBrO_3$

In these titrations it is evident that with the addition of the titrant the E.M.F. rose steadily till the equivalence point. At the equivalence point there was a sharp jump in potential followed by a steady rise in each case.

From the amount of ceric sulphate used, corresponding to the equivalence point in each titration, the amount of ferrous ethylenediamine sulphate required for the reduction of each substance was calculated and consequently the amount of each substance was determined. The results recorded in Tables II-VIII show that potassium permanganate, ceric sulphate, potassium chlorate, hydrogen peroxide, potassium persulphate, potassium dichromate and potassium bromate can be determined indirectly by the potentiometric method, using ferrous ethylenediamine sulphate (FES) as a reducing agent.

TABLE II

POTASSIUM PERMANGANATE

$KMnO_4$ taken g	*0.05N FES added ml*	*0.05N $Ce(SO_4)_2$ used for excess FES ml*	*0.05N FES used by $KMnO_4$ ml*	*$KMnO_4$ found g*
0.0120	16.00	8.33	7.67	0.0121
0.0151	20.00	10.38	9.62	0.0152
0.0221	28.00	14.04	13.96	0.0221
0.0344	44.00	22.18	21.82	0.0345
0.0398	50.00	24.83	25.17	0.0398

TABLE III

CERIC SULPHATE

$Ce(SO_4)_2$ taken g	*0.05N FES added ml*	*0.05N $Ce(SO_4)_2$ used for excess FES ml*	*0.05N FES used by $Ce(SO_4)_2$ ml*	*$Ce(SO_4)_2$ found g*
0.1199	15.00	7.78	7.22	0.1200
0.1671	20.00	9.93	10.07	0.1673
0.2221	26.00	12.63	13.37	0.2221
0.2734	32.00	15.53	16.47	0.2735
0.3141	38.00	19.08	18.92	0.3142

TABLE IV

POTASSIUM CHLORATE

$KClO_3$ *taken* *g*	*0.05N FES* *added* *ml*	*0.05N $Ce(SO_4)_2$ used for excess FES* *ml*	*0.05N FES used by $KClO_3$* *ml*	$KClO_3$ *found* *g*
0.0069	14.00	7.13	6.87	0.0070
0.0132	26.00	13.23	12.77	0.0131
0.0164	32.00	15.98	16.02	0.0164
0.0201	38.00	18.46	19.54	0.0200
0.0213	42.00	20.98	21.02	0.0214

TABLE V

HYDROGEN PEROXIDE

H_2O_2 *taken* *g*	*0.05N FES* *added* *ml*	*0.05N $Ce(SO_4)_2$ used for excess FES* *ml*	*0.05N FES used by H_2O_2* *ml*	H_2O_2 *found* *g*
0.0036	10.00	5.78	4.22	0.0036
0.0071	20.00	11.63	8.37	0.0071
0.0128	30.00	14.78	15.22	0.0129
0.0160	38.00	19.13	18.87	0.0160
0.0198	46.00	22.68	23.32	0.0198

TABLE VI

POTASSIUM PERSULPHATE

$K_2S_2O_8$ *taken* *g*	*0.05N FES* *added* *ml*	*0.05N $Ce(SO_4)_2$ used for excess FES* *ml*	*0.05N FES used by $K_2S_2O_8$* *ml*	$K_2S_2O_8$ *found* *g*
0.0511	15.00	7.44	7.56	0.0511
0.0656	20.00	10.28	9.72	0.0657
0.0986	30.00	15.39	14.61	0.0987
0.1185	36.00	18.48	17.52	0.1184
0.1326	40.00	20.37	19.63	0.1327

TABLE VII

POTASSIUM DICHROMATE

$K_2Cr_2O_7$ *taken* *g*	*0.05N FES* *added* *ml*	*0.05N $Ce(SO_4)_2$ used for excess FES* *ml*	*0.05N FES used by $K_2Cr_2O_7$* *ml*	$K_2Cr_2O_7$ *found* *g*
0.0107	10.00	5.58	4.42	0.0108
0.0263	20.00	9.24	10.76	0.0264
0.0412	32.00	15.17	16.83	0.0412
0.0443	38.00	19.88	18.12	0.0444
0.0526	44.00	22.48	21.52	0.0527

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TABLE VIII

POTASSIUM BROMATE

$KBrO_3$ taken g	0.05N FES added ml	0.05N $Ce(SO_4)_2$ used for excess FES ml	0.05N FES used by $KBrO_3$ ml	$KBrO_3$ found g
0.0068	10.00	5.08	4.92	0.0068
0.0112	16.00	7.83	8.17	0.0113
0.0177	26.00	13.17	12.83	0.0178
0.0260	38.00	19.24	18.76	0.0261
0.0335	48.00	23.93	24.07	0.0335

SUMMARY

Ferrous ethylenediamine sulphate has been used as a reducing agent to determine indirectly potassium permanganate, ceric sulphate, potassium chlorate, hydrogen peroxide, potassium persulphate, potassium dichromate and potassium bromate by a potentiometric method. An excess of ferrous ethylenediamine sulphate added to each of the substances in acid medium was titrated with a standard solution of ceric sulphate, using platinum foil as an oxidation-reduction electrode coupled with a saturated calomel electrode through an agar-agar potassium chloride bridge.

RÉSUMÉ

Le sulfate double de fer(II) et d'éthylènediamine est proposé comme réducteur pour le dosage potentiométrique indirect du permanganate de potassium, du sulfate de cérium(IV), du peroxyde d'hydrogène, des persulfate, dichromate et bromate de potassium. L'excès de sulfate double de fer(II) et d'éthylènediamine ajouté à chacune de ces substances, en milieu acide, est titré au moyen d'une solution étalon de sulfate de cérium(IV); on utilise une feuille de platine comme électrode d'oxydo-réduction, reliée à une électrode au calomel saturée par un pont d'agar-agar-chlorure de potassium.

ZUSAMMENFASSUNG

Das Eisen(II)äthylendiaminsulfat wird als Reduktionsmittel für die indirekten potentiometrischen Bestimmungen von Kaliumpermanganat, Cer(IV)sulfat, Wasserstoffperoxyd, Kaliumpersulfat, -bromat und -dichromat vorgeschlagen. Der zu jeder der Substanzen in saurer Lösung zugegebene Überschuss an Eisen(II)äthylendiaminsulfat wird mit einer Vergleichslösung von Cer(IV)sulfat titriert. Man verwendet eine Platinfolie als Oxydation-Reduktions-Elektrode, welche mit einer gesättigten Kalomelelektrode mittels einer Agar-Agar-Kaliumchlorid-Brücke verbunden ist.

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OXIDATIONS WITH ALKALINE PERMANGANATE USING MONOVALENT THALLIUM FOR THE BACK TITRATION

IV. ESTIMATION OF HYDROGEN PEROXIDE

by

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Hydrogen peroxide is determined in two ways, directly and indirectly. The direct methods consist in the titration of hydrogen peroxide with potassium permanganate[1], with iodate[2] (after oxidation with hypoiodic acid) or with ceric solutions[3].

The indirect method[4] consists in treating hydrogen peroxide with an excess of hypobromite solution and titrating the excess hypobromite with arsenious oxide.

Hydrogen peroxide is known to reduce potassium permanganate in alkaline medium but the reaction was not studied quantitatively. The present investigation deals with this problem and a method is developed for the potentiometric determination of hydrogen peroxide with alkaline permanganate.

EXPERIMENTAL

Hydrogen peroxide solution was prepared by the appropriate dilution of AnalaR grade sample, with twice-distilled water. The concentration of the solution was determined by titration with potassium permanganate in presence of $\sim 1N$ H_2SO_4[1]. This solution was fairly stable and suffered only very slight decomposition ($\sim 4\%$) over a period of 3 days.

The other solutions, *viz.* monovalent thallium and permanganate, were prepared and standardized as previously described[5].

RESULTS

In studying this reaction we followed the same lines given in the previous investigations, *viz.* titration of potassium permanganate with hydrogen peroxide and oxidation of hydrogen peroxide with excess permanganate, followed by titration of the excess permanganate with monovalent thallium.

(1) *Titration of hydrogen peroxide with potassium permanganate*

In these titrations we were unable to obtain good results, owing apparently to the instability of hydrogen peroxide in alkaline medium. Decomposition of hydrogen peroxide was also catalysed by the precipitated manganese dioxide[6]. The end-points were always attained $\sim 70\%$ earlier than the theoretical ones. We then performed the reaction in presence of telluric acid which was thought to yield good results owing to its solvent action on manganese dioxide, but then the end-points were attained 45% earlier than the theoretical values. Trials to stabilize hydrogen peroxide by sodium pyrophosphate[7] or sodium silicate[8] did not lead to good results (*cf.* Table I).

TABLE I

TITRATION OF 5 ml H_2O_2 IN 0.1*N* NaOH WITH 0.1136*N* $KMnO_4$

Normality of H_2O_2	*Max. inflection per 0.1 ml* $KMnO_4$ *mV*	*Theoretical end-point ml*	*Experimental end-point ml*	*Error %*	*Other conditions*
0.0563	220	4.13	1.14	—72.4	
0.0563	205	4.13	1.24	—70.0	Sodium pyrophosphate
0.0563	135	4.13	2.15	—47.94	Telluric acid added
0.0563	205	4.13	2.27	—45.04	Telluric acid + sod. pyrophosphate
0.1074 (2.5 ml)	130	3.94	1.73	—56.09	Telluric acid + sod. silicate

In the absence of telluric acid, constant potentials were not readily attained; the potential rose slowly after the addition of $KMnO_4$ and separation of MnO_2, taking 2-4 minutes to become steady. Gas bubbles were always visible on the surface of the solid. However, in the presence of telluric acid the potentials rapidly acquired steady values after ∼1 min. In this latter case no manganese dioxide separated out but it is supposed that the catalytic effect of MnO_2 on the decomposition of H_2O_2 occurs on immediate addition of $KMnO_4$ before it becomes complexed with telluric acid. A titration curve representing the states of affairs is shown in Fig. 1.

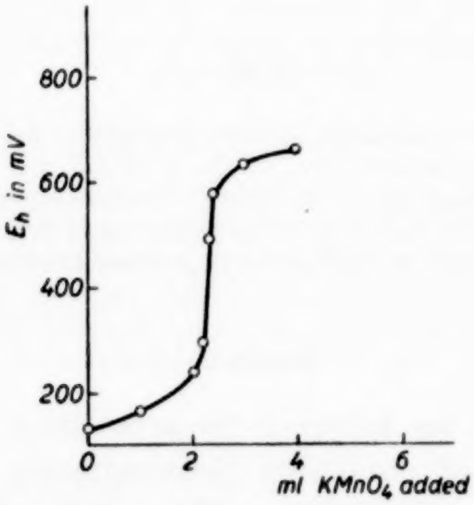

Fig. 1. Titration of 10 ml 0.0563*N* H_2O_2 in 0.1*N* NaOH with 0.1136*N* $KMnO_4$.

(2) *Titration of potassium permanganate with hydrogen peroxide*

Owing to the strong reducing action of hydrogen peroxide, reduction of permanganate passes rapidly to MnO_2. Even in the presence of Ba^{+2} ions (equivalent to four times the permanganate present) the end-points could not be checked at the manganate state. The end-points are nearly always attained later than the theoretical values, even when dilute hydrogen peroxide solutions are used (see Table II). It was then found impracticable to work in the presence of Ba^{+2} ions. The titration curves under these conditions possess only one single inflection which, although sharp, occurs later than the theoretical end-points.

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TABLE II

TITRATION OF $KMnO_4$ IN PRESENCE OF TELLURIC ACID WITH H_2O_2

Alkalinity	*Max. inflection per 0.1 ml H_2O_2 mV*	*Theoretical end-point ml*	*Experimental end-point ml*	*Error %*
Titration of 5 ml $0.1136N$ $KMnO_4$ with $0.08236N$ H_2O_2				
$1N$ NaOH	201	4.13	4.14	+0.24
$1N$ NaOH*	267	4.13	4.12	—0.24
$3N$ NaOH	195	4.13	4.12	—0.24
Titration of 5 ml $0.1136N$ $KMnO_4$ with $0.0811N$ H_2O_2				
$0.5N$ NaOH	138	4.20	4.22	+0.48
$2N$ NaOH	116	4.20	4.22	+0.48
$3N$ NaOH*	156	4.20	4.215	+0.36
Titration of 5 ml $0.02272N$ $KMnO_4$ with $0.00811N$ H_2O_2				
$0.5N$ NaOH*	80	8.4	8.43	+0.36
$0.5N$ NaOH	64	8.4	8.43	+0.36

* Sodium pyrophosphate added to the reaction mixture.

When the reaction is performed in absence of both Ba^{+2} ions and telluric acid, end-points later than the theoretical values are encountered. This is possibly brought about by the catalytic decomposition of a small portion of H_2O_2 by the precipitated manganese dioxide before it reacts with the higher oxidation states of manganese. However, in presence of telluric acid, in which case manganese dioxide did not separate out, end-points coinciding with the calculated ones are attained. The results are good for concentrations of H_2O_2 varying from $0.08236N$ to $0.00811N$ and for alkalinities ranging between 0.5-$3N$. The titration curves are smooth and characterized by two inflections. The first inflection corresponds to the manganate state and occurs much later than the theoretical value while the second corresponds to MnO_2 and occurs in the region of the theoretical end-point. The latter inflections are sharp, amounting to $\sim$200 mV in the case of $0.1N$ solutions.

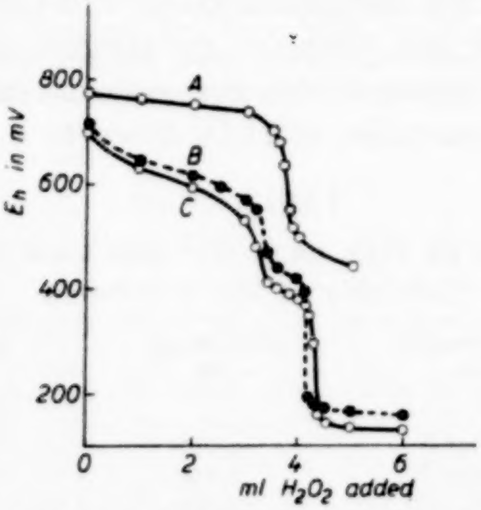

Fig. 2. (A) Titration of 10 ml $0.1136N$ $KMnO_4$ in $1N$ NaOH + Ba^{+2} ions with $0.08236N$ H_2O_2;
(B) Titration of 5 ml $0.1136N$ $KMnO_4$ in $1N$ NaOH + telluric acid + sodium pyrophosphate with $0.08236N$ H_2O_2;
(C) Titration of 5 ml $0.1136N$ $KMnO_4$ in $1N$ NaOH with $0.08236N$ H_2O_2.

The time necessary for equilibrium varies from stage to stage. At the beginning of the titration when the reaction involves reduction of $KMnO_4$, the equilibrium is rapid. Beyond the first inflection it takes ∼ 3 min in the presence and 5 min in the absence of telluric acid.

TABLE III

TITRATION OF $KMnO_4$ WITH H_2O_2 IN ABSENCE OF TELLURIC ACID

Alkalinity	*Max. inflection per 0.1 ml H_2O_2 mV*	*Theoretical end-point ml*	*Experimental end-point ml*	*Error %*
Titration of 5 ml 0.1136*N* $KMnO_4$ with 0.08236*N* H_2O_2 in absence of Ba^{+2} ions.				
1*N* NaOH*	105	4.13	4.32	+ 4.60
1*N* NaOH	184	4.13	4.34	+ 5.08
Titration of 5 ml 0.02272*N* $KMnO_4$ with 0.00811*N* H_2O_2 in absence of Ba^{+2} ions				
0.5*N* NaOH	61	8.4	8.63	+ 2.74
Titration of 10 ml 0.1136*N* $KMnO_4$ in presence of Ba^{+2} ions with H_2O_2				
1*N* NaOH**	82	2.81	3.74	+33.09
1*N* NaOH***	57	8.43	10.87	+28.94

* Sodium pyrophosphate added to the reaction mixture.
** Normality of H_2O_2 solution 0.0809.
*** ,, ,, ,, ,, 0.02697.

(3) *Oxidation of hydrogen peroxide by permanganate and back titrating excess oxidant with monovalent thallium*

From the foregoing study it becomes apparent that reduction of $KMnO_4$ in presence of Ba^{+2} ions does not give quantitative results on account of the fact that the reaction product is not one definite compound. The accuracy of the results in the presence of telluric acid makes it possible to develop an indirect method for the estimation of hydrogen peroxide consisting of the oxidation of H_2O_2 with excess $KMnO_4$ and titration of the excess oxidant with monovalent thallium. Since reduction of permanganate does not pass beyond the quadrivalent manganese stage in the presence of excess $KMnO_4$, it is not necessary to add H_2O_2 slowly as is the case when the reduction is to be checked at the manganate stage. It is sufficient to stir the solution in order to mix the reactants and, owing to the rapidity of the reaction, the excess oxidant can be immediately titrated with monovalent thallium. The method yields accurate results for small quantities of H_2O_2 down to 0.3 mg.

TABLE IV

DETERMINATION OF H_2O_2 USING Tl^+ FOR BACK TITRATION

Normality of Tl^+ = 0.0295

Vol. and Normality of $KMnO_4$	*Vol. and Normality of H_2O_2*	*H_2O_2 present mg*	*H_2O_2 found mg*	*Error %*
5 ml 0.1084*N*	3 ml 0.0941*N*	4.799	4.819	+0.42
5 ,, 0.1084*N*	2 ,, 0.0941*N*	3.199	3.185	—0.44
5 ,, 0.1084*N*	1 ,, 0.0941*N*	1.600	1.606	+0.38
10 ,, 0.02168*N*	3 ,, 0.01882*N*	0.960	0.960	nil
10 ,, 0.02168*N*	2 ,, 0.01882*N*	0.640	0.637	—0.47
10 ,, 0.02168*N*	1 ,, 0.01882*N*	0.320	0.318	—0.63

SUMMARY

Owing to the instability of hydrogen peroxide in alkaline solutions, direct oxidation with $KMnO_4$ did not yield accurate results. The back titration of $KMnO_4$ in the presence of 1*N* NaOH and Ba^{+2} ions also gave inaccurate results. The reaction could not be checked at the manganate state. However, in the presence of 2*N* NaOH and telluric acid quantitative data were obtained, which is not the case if telluric acid is absent.

Another advantageous method is the oxidation of hydrogen peroxide with excess $KMnO_4$ in the presence of 1*N* NaOH and telluric acid, followed by back titrating excess oxidant with monovalent thallium.

RÉSUMÉ

Vu l'instabilité du peroxyde d'hydrogène en solution alcaline, l'oxydation directe par $KMnO_4$ ne donne pas de résultats précis. Le titrage de l'excès de $KMnO_4$, en présence de NaOH *N* et d'ions Ba^{+2}, donne aussi des résultats peu précis, la réaction ne pouvant être contrôlée au stade manganate. Par contre, en présence de NaOH 2*N* et d'acide tellurique, des résultats quantitatifs sont obtenus, ce qui n'est pas le cas en l'absence d'acide tellurique. La méthode consistant à oxyder H_2O_2 par un excès de $KMnO_4$, en présence de NaOH *N* et d'acide tellurique, et à titrer l'excès d'oxydant au moyen du thallium (I) présente aussi des avantages.

ZUSAMMENFASSUNG

Da Wasserstoffperoxyd in alkalischer Lösung sehr unbeständig ist, gab die direkte Oxydation mit $KMnO_4$ keine genauen Resultate. Die Rücktitration von $KMnO_4$ in Gegenwart von *N* NaOH und Ba^{+2}-Ionen ergab ebenfalls ungenaue Resultate. Die Reaktion konnte nicht im Manganat-Stadium geprüft werden. Wenn jedoch 2*N* NaOH und Tellursäure zugegeben werden, erhält man quantitative Resultate, was nicht der Fall ist, wenn Tellursäure nicht zugegeben wird. Eine andere vorteilhafte Methode besteht darin, die Oxydation von Wasserstoffperoxyd mit $KMnO_4$ in Gegenwart von *N* NaOH und Tellursäure vorzunehmen, und dann den Überschuss des Oxydationsmittels mit einwertigem Thallium zurückzutitrieren.

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OXIDATIONS WITH ALKALINE PERMANGANATE USING MONOVALENT THALLIUM FOR THE BACK TITRATION

V. ESTIMATION OF HYDRAZINE

by

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The volumetric estimation of hydrazine is based on its tendency to become oxidized to nitrogen and water. Oxidizing agents usually used are iodate[1,2], bromate[2] or iodine[3].

Oxidation of hydrazine is a complex problem as it gives rise to various products in addition to nitrogen and water *e.g.* ammonia or hydrazoic acid. According to HIGGINSON, SUTTON AND WRIGHT[4], the consumption of oxidizing agent per mol of hydrazine will be lower if hydrazine is kept in excess than if the oxidizing agent is kept in excess. This suggests that direct titration of hydrazine by oxidizing agents gives rise to lower results whereas the reverse process of titration leads to accurate values. The direct oxidation of hydrazine by potassium permanganate in alkaline medium has not yet been applied as an analytical method and it is the aim of the present investigation to deal with this subject.

EXPERIMENTAL

Hydrazine solutions are prepared from hydrazine sulphate, by dissolving the AnalaR product in twice-distilled water. The concentration of hydrazine was determined by the iodate method, using chloroform as a solvent for the liberated iodine.

The permanganate solutions are prepared according to the method of STAMM[5] and standardized by the acid oxalate method[6]. The experimental technique and procedure is the same as described previously[7].

RESULTS

Oxidation of hydrazine with permanganate

Hydrazine is a strong reducing agent in alkaline medium if the process involves the formation of nitrogen and water. The E_0 value of the system N_2H_4/N_2 amounts to −1.16[8] volt at unit $[OH^-]$. This potential together with that of the MnO_4^-/MnO_2 couple[8] corresponds to an equilibrium constant and a degree of completion amounting to $3 \cdot 10^{-366}$ and $1.6 \cdot 10^{-51}$ respectively for the reaction between permanganate and hydrazine in alkaline solutions.

The results obtained on directly titrating hydrazine with $KMnO_4$ are shown in Table I and represented graphically in Fig. 1. The data indicate that the end-points are attained much earlier than the theoretical values owing to the tendency of hydrazine to become oxidized by atmospheric oxygen in alkaline solutions[9]. Atmos-

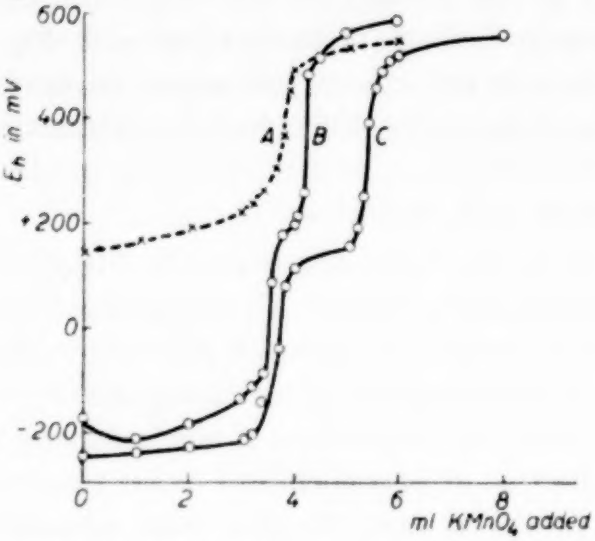

Fig. 1. (A) Titration of 10 ml 0.004548*N* N_2H_4 with 0.01084*N* $KMnO_4$ in the presence of telluric acid;
(B) Titration of 10 ml 0.04548*N* N_2H_4 with 0.1084*N* $KMnO_4$ in the absence of telluric acid;
(C) Titration of 10 ml 0.04548*N* N_2H_4 with 0.1084*N* $KMnO_4$ in the presence of telluric acid.

pheric oxidation is largely enhanced in presence of quadrivalent manganese as found experimentally. Thus it was observed that in unstirred solutions only 1% of hydrazine was decomposed after a period of one hour. On stirring 5% were decomposed after 15 min, the time taken to attain the first inflection, in the titration of hydrazine with permanganate. Oxidation of hydrazine was more enhanced in presence of the Mn^{+4}– tellurate complex prepared by mixing together equivalent amounts of hydrazine and $KMnO_4$ in the presence of telluric acid and 0.1*N* NaOH. Fig. 1 shows that in case of the more concentrated solutions titrated (0.04548*N*), the titration curves are characterized by two inflections. It is most probable that in the more concentrated solutions the reaction takes place in two steps, but the mechanism of the reaction is not clear in view of the decomposition of hydrazine.

TABLE I

TITRATION OF 10 ml 0.04548*N* HYDRAZINE WITH 0.1084*N* $KMnO_4$

Atmosphere	*Max. inflection* *1st step mV*	*2nd step mV*	*Theoretical end-point* $N_2H_4 \rightarrow N_2 + H_2O$ *ml*	*Exptl. end-point* *1st step ml*	*2nd step ml*	*Error 2nd step %*
Air	143	217	7.41	3.3	4.13	—44.26
,,	170	236	7.41	3.45	4.22	—43.05
,,	100	140	7.41	3.6	5.36	—27.67
Nitrogen	70	152	7.41	3.5	5.65	—23.75
,,	58	163	7.41	3.6	5.73	—22.67
Hydrogen	70	156	7.41	4.5	6.57	—6.57

It is noteworthy to state that during the first step a white precipitate is produced if telluric acid is present which then redissolves to give a clear orange red solution at the second end-point. A white precipitate is also formed when hydrazine is mixed with an alkaline solution containing telluric acid and quadrivalent manganese.

The white precipitate is not formed on titrating 0.004548*N* N_2H_4 solutions and the curve is characterized by a single inflection (curve A, Fig. 1). The end-points are attained much earlier than in the case of the more concentrated solutions owing to the increased instability of the more dilute hydrazine solution in presence of alkali.

Reduction of permanganate with hydrazine

In contradistinction from the foregoing reaction, titration of permanganate with hydrazine should give quantitative results. The presence of excess oxidant apparently favours the oxidation of hydrazine to nitrogen and water. According to HIGGINSON, SUTTON AND WRIGHT[4] the consumption of oxidizing agent per mole of hydrazine will be lower if hydrazine is kept in excess than if the oxidizing agent is kept in excess.

In these titrations reduction of permanganate takes place normally, *i.e.* in absence of Ba^{+2} ions MnO_2 is produced and the end-point coincides with the theoretical value irrespective of whether telluric acid is present or absent. In the presence of Ba^{+2} ions equivalent (or twice the equivalent) to permanganate, reduction of the latter is checked at the manganate state. Under these conditions and taking $E^\circ_{(HO)}MnO_4^-/MnO_4^{-2} = 0.564$ and $E^\circ_{(HO)}N_2H_4/N_2$ couple $= -1.16$ volt, the equilibrium constant and the degree of completion for the reaction $4\,Mn^{+7} + N_2H_4 + 4\,OH^- \rightarrow 4\,Mn^{+6} + N_2 + 4\,H_2O$ amount to $1.3 \cdot 10^{-117}$ and $4.2 \cdot 10^{-24}$ respectively.

TABLE IIA

TITRATION OF PERMANGANATE WITH HYDRAZINE IN THE ABSENCE OF Ba^{+2} IONS

Alkalinity	*Max. inflection 0.1 ml hydrazine soln. mV*	*Theoretical end-point ml*	*Exptl. end-point ml*	*Error %*
Titration of 5 ml 0.1084*N* $KMnO_4$ with 0.04548*N* hydrazine				
0.5*N* NaOH*	214	7.15	7.17	+0.27
1*N* ,,	138	7.15	7.14	—0.14
2*N* ,, *	207	7.15	7.18	+0.41
2.5*N* ,,	122	7.15	7.13	—0.27
Titration of 5 ml 0.0542*N* $KMnO_4$ with 0.01137*N* hydrazine				
0.5*N* NaOH	22	14.3	14.27	—0.21
1*N* ,,	21	14.3	14.25	—0.35
1*N* ,, *	44	14.3	14.25	—0.35

* Telluric acid added to reaction mixture.

TABLE IIB

REDUCTION OF PERMANGANATE WITH HYDRAZINE IN THE PRESENCE OF Ba^{+2} IONS

Alkalinity	*Max. inflection 0.1 ml hydrazine soln. mV*	*Theoretical end-point ml*	*Exptl. end-point ml*	*Error %*
Titration of 5 ml 0.1084*N* $KMnO_4$ with 0.04548*N* hydrazine				
1*N* NaOH	160	2.38	2.37	—0.42
0.75*N* ,,	159	2.38	2.37	—0.42
Titration of 5 ml 0.0542*N* $KMnO_4$ with 0.01137*N* hydrazine				
1*N* NaOH	137	4.76	4.74	—0.42
0.75*N* ,,	126	4.76	4.77	+0.21

References p. 582

In the presence of Ba^{+2} ions the titration curve (curve A, Fig. 2) is characterized by a single inflection, whereas in its absence two inflections are observed (curve B, Fig. 2). The first of these corresponding to the manganate state is very poor and occurs later than the theoretical value, while the second corresponding to the manganese dioxide is very sharp and coincides with the theoretical value. In both cases the reaction is rapid.

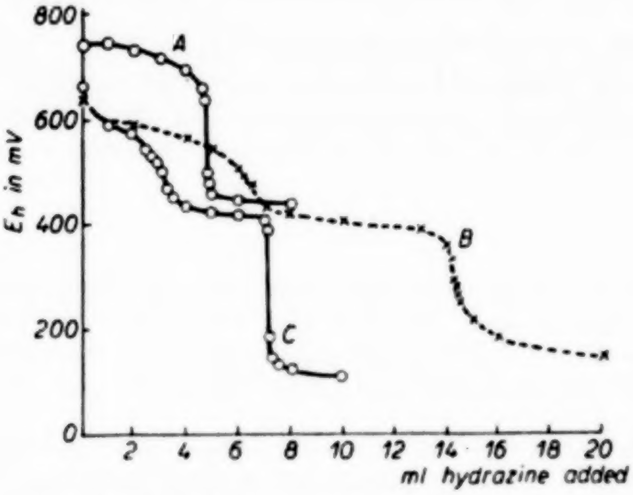

Fig. 2. (A) Titration of 5 ml 0.0542N $KMnO_4$ in 1N NaOH with 0.01137N N_2H_4 in the presence of Ba^{+2} ions;
(B) Titration of 5 ml 0.0542N $KMnO_4$ in 1N NaOH with 0.01137N N_2H_4 in the absence of Ba^{+2} ions;
(C) Titration of 5 ml 0.1084N $KMnO_4$ in 2N NaOH with 0.04548N N_2H_4 in the absence of Ba^{+2} ions.

Determination of hydrazine using monovalent thallium for back titration of excess permanganate

The above facts can be made use of in the determination of hydrazine by mixing with excess permanganate and back titrating excess oxidant with monovalent thallium. The process can be performed in the presence of Ba^{+2} ions, whereby reduction of $KMnO_4$ is checked at the manganate state. In this case the addition of hydrazine

TABLE III

DETERMINATION OF HYDRAZINE USING Tl^+ FOR BACK TITRATION OF PERMANGANATE

$Tl^+ = 0.0295N$, NaOH = 1N

Vol. and Normality of $KMnO_4$	*Vol. and Normality of hydrazine*	*Hydrazine added mg*	*Hydrazine found mg*	*Error %*
5 ml 0.1048N*	5 ml 0.04548N	1.822	1.819	—0.17
5 ,, 0.1048N*	3 ,, 0.04548N	1.093	1.098	+0.46
5 ,, 0.1048N**	2 ,, 0.04548N	0.730	0.732	+0.27
5 ,, 0.1048N**	1 ,, 0.04548N	0.364	0.365	+0.27
5 ,, 0.1048N*	1 ,, 0.04548N	0.364	0.362	—0.55
5 ,, 0.0524N*	5 ,, 0.01137N	0.455	0.453	—0.44
5 ,, 0.0524N*	2 ,, 0.01137N	0.182	0.183	+0.55
5 ,, 0.0524N**	2 ,, 0.01137N	0.182	0.181	—0.55

* Titration carried out in presence of telluric acid.
** Titration performed in presence of Ba^{+2} ions.

should be made slowly and with constant stirring to avoid reduction of $KMnO_4$ below the manganate state.

The estimation can also be made in the absence of Ba^{+2} ions when reduction of permanganate passes to quadrivalent manganese. This process should be performed in the presence of telluric acid since although quantitative reduction of $KMnO_4$ occurs in the absence of telluric acid by hydrazine, this is not the case with monovalent thallium. With this latter reagent telluric acid should be present to prevent the formation of lower oxides of manganese[10].

The results shown in Table III indicate that the process is applicable to small amounts of hydrazine as low as 0.182 mg.

SUMMARY

Oxidation of hydrazine in alkaline solutions with $KMnO_4$ gives inaccurate results both in the presence of absence of telluric acid. The titration curve is characterized by two inflections.

Titration of $KMnO_4$ with hydrazine gives good results in the presence of Ba^{+2} ions and 0.75-1N NaOH (when MnO_4^- gives MnO_4^{-2}) or in the presence of 0.5-2.5N NaOH only (when MnO_4^- gives MnO_2).

Hydrazine could be estimated by oxidation with $KMnO_4$ either in the presence of Ba^{+2} ions or telluric acid, after which the excess permanganate is back titrated with monovalent thallium. The alkalinity is kept at 1N NaOH.

RÉSUMÉ

L'oxydation de l'hydrazine, en solution alcaline, au moyen de $KMnO_4$ donne des résultats peu précis, en présence ou en l'absence d'acide tellurique. Les courbes de titrage sont caractérisées par deux inflexions. Le titrage de $KMnO_4$ par l'hydrazine donne de bons résultats, en présence de Ba^{+2} et de NaOH 0.75 à 1N (dans ce cas MnO_4^- se réduit en MnO_4^{-2}), ou en présence de NaOH 0.5 à 2.5N seulement (dans ce cas MnO_4^- se réduit en MnO_2). L'hydrazine peut être dosée par addition d'un excès de $KMnO_4$, en présence de NaOH N, on titre ensuite l'excès d'oxydant par le thallium(I).

ZUSAMMENFASSUNG

Die Oxydation von Hydrazin in alkalischer Lösung mit $KMnO_4$ gab ungenaue Ergebnisse sowohl in Gegenwart als auch in Abwesenheit von Tellursäure. Die Titrationskurve weist zwei Inflektionspunkte auf. Die Titration von $KMnO_4$ mit Hydrazin gibt gute Resultate; in Gegenwart von Ba^{+2} Ionen und 0.75-1N NaOH wird MnO_4^- zu MnO_4^{-2} reduziert; in Gegenwart von 0.5-2.5N NaOH allein, bildet sich MnO_2 aus MnO_4^-. Hydrazin kann bestimmt werden durch Oxydation mit $KMnO_4$ in Gegenwart von Ba^{+2}-Ionen oder von Tellursäure, und Rücktitration von überschüssigem Permanganat mit einwertigem Thallium. Die Alkalinität wird auf 1N NaOH gehalten.

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A POTENTIOMETRIC DETERMINATION OF POTASSIUM ETHYL XANTHATE

by

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INTRODUCTION

It is known, that xanthates in general, react with Cu^{+2} to give insoluble Cu-xanthate-compounds, according to

$$2\,C_2H_5\text{-O-CS.SK} + Cu^{+2} \rightarrow (C_2H_5\text{-O-CS.S})_2Cu\downarrow + 2\,K^+.$$

Xanthates may be formed by the reaction of carbon disulphide with an alkanol in alkaline medium. If both reactions are sufficiently rapid and quantitative and if it is possible to determine the end-point of the reaction of a xanthate with Cu^{+2} accurately, carbon disulphide may be determined quantitatively using both reactions. To answer these questions, it was investigated, whether xanthate can be titrated potentiometrically with Cu^{+2}. In this investigation use will be made of potassium ethyl xanthate, formed by the reaction of carbon disulphide and ethanolic KOH.

EXPERIMENTAL

A standard solution of potassium ethyl xanthate was prepared by weighing about 0.8 g of pure carbon disulphide to the nearest 0.1 mg in a sealed, thin-walled glass tube, and placing this tube in a solution of 0.1 *N* ethanolic KOH, breaking the tube by shaking, and making up to 100 ml by addition of 0.1 *N* ethanolic KOH. A 50-ml aliquot of this solution was diluted to 1 l with 0.1 *N* ethanolic KOH. This solution thus contains about 0.4 mg of CS_2 per ml.

From preliminary experiments it could be shown, that when an aliquot of this standard solution is titrated potentiometrically with a solution of Cu(II)-acetate, which contains acetic acid, using a copper electrode as an indicator electrode and a saturated calomel electrode as a reference electrode, a sharp E.M.F.-drop occurs at the end-point of the reaction. To establish whether precise and accurate results could be obtained in this way, a number of determinations was carried out in the following way:

Aliquots of the standard solution were diluted with water to about 200 ml. This solution was titrated potentiometrically with 0.02 *N* Cu(II)-acetate solution which contained 140 ml of 4 *N* acetic acid per l. A copper electrode was used as an indicator electrode and a saturated calomel electrode as a reference electrode. The E.M.F. was measured with a Beckman pH-meter, model H 2.

24 Determinations were carried out on three different quantities of the standard solution. The average results are given in Table I. In this table CS_2 calc. is calculated assuming that CS_2 reacts quantitatively with ethanolic KOH to give potassium ethyl xanthate. The end-point of the titration is calculated with the aid of the second derivative of E.M.F. to ml of standard Cu-solution consumed. The precision is expressed in terms of the standard deviation in mg of CS_2.

The combined standard deviation is 0.038 mg of CS_2 so that the precision is to be considered satisfactory. When the differences found are tested statistically using the *t*-test, it is found, that only for the smallest quantity of CS_2 accurate results are obtained. In both other cases the results are significantly low.

TABLE I

CS_2 calc.	*CS_2 found*	*Difference*	*Standard dev.*	*Number of detns.*
2.074 mg	2.076 mg	+0.002 mg	0.037 mg	8
4.149 ,,	4.112 ,,	—0.037 ,,	0.026 ,,	8
8.298 ,,	8.209 ,,	—0.089 ,,	0.046 ,,	8

Since the xanthate solution may become acid by additon of the acid Cu-solution and since it is known, that xanthates decompose in acid medium, the pH at the equivalence point was measured in all three cases.

Table II shows the values found.

TABLE II

CS_2 calc.	pH *at the end-point*
2.074 mg	9.0
4.149 ,,	4.3
8.298 ,,	4.2

The large discrepancy in pH values in Table II suggests that the low results are indeed due to decomposition of the xanthate. To establish the relation between pH of the xanthate solution at the equivalence point and the quantity of CS_2 found by titration, buffered solutions of potassium ethyl xanthate were titrated potentiometrically with a solution of 0.02*N* Cu(II)-acetate, which was as low as 0.02*N* in acetic acid to minimize the influence of the acid in the standard Cu-solution on the final pH. The results are given in Table III.

TABLE III

CS_2 calc.	*CS_2 found*	*CS_2 lost*	pH
6.425 mg	6.445 mg	—0.020 mg	5.8
	6.170 ,,	—0.255 ,,	5.5
	5.972 ,,	—0.453 ,,	5.0
	5.176 ,,	—1.249 ,,	4.5
	5.053 ,,	—1.372 ,,	4.0

From this table it is seen that the xanthate decomposes below pH 5.8. This means that during the titration the pH of the solution should not become lower than 5.8. On the other hand, the pH should not exceed 7.0 in order to prevent the precipitation of cupric hydroxide. It was found that in titration of solutions previously buffered between pH = 7.0 and pH = 5.8 the E.M.F.-drop at the equivalence point is rather small, thus reducing the precision of the end-point determination.

It is necessary therefore to titrate with a Cu(II)-acetate solution, which contains a very small amount of acetic acid and neutralize the xanthate solution with acetic acid prior to titration.

On these considerations a recommended procedure has been developed.

RECOMMENDED PROCEDURE

Neutralize the solution of potassium ethyl xanthate in ethanolic KOH, containing 1 to 10 mg of CS_2, with 0.1*N* acetic acid to pH = 7.0, using a pH-meter. With constant stirring titrate potentiometrically with 0.02*N* Cu(II)-acetate solution, which contains 6 ml of 1*N* acetic acid per l, using a copper electrode as an indicator electrode and a saturated calomel electrode as a reference electrode. If possible, apply a counter-voltage of 0.5 to 1.0 V, because the sign of the E.M.F. reverses during the titration. Calculate the end-point with the aid of the second derivative of the E.M.F. to ml of standard Cu-solution consumed.

Standardize the Cu(II)-acetate standard solution by electrolytic determination of the Cu-content of the Cu(II)-acetate in the preparation of the standard solution.

RESULTS

Following this procedure 12 determinations were carried out starting from three different quantities of potassium ethyl xanthate. The average results are given in Table IV.

TABLE IV

CS_2 calc.	*CS_2 found*	*Difference*	*Standard dev.*	*Number of detns.*
1.980 mg	1.974 mg	—0.006 mg	0.056 mg	4
3.961 ,,	3.943 ,,	—0.018 ,,	0.026 ,,	4
7.922 ,,	7.902 ,,	—0.020 ,,	0.038 ,,	4

The combined standard deviation is 0.042 mg of CS_2. From Table IV it is seen that the precision is very satisfactory again. When the standard deviations shown in Table I are compared with those shown in Table IV, it proves that the pH does not significantly influence the standard deviation. Therefore the standard deviations shown in Table I and Table IV are combined to obtain a better estimate of the true standard deviation. The combined standard deviation is 0.039 mg of CS_2.

The *t*-test applied to the average difference indicated that there is no reason to assume that the amount of carbon disulphide found deviates significantly from the amount present; with the null hypothesis that there is no difference the probability of our findings is 0.25. The E.M.F.-drop at the end-point in this case is about 86 mV; the titration curve is represented in Fig. 1.

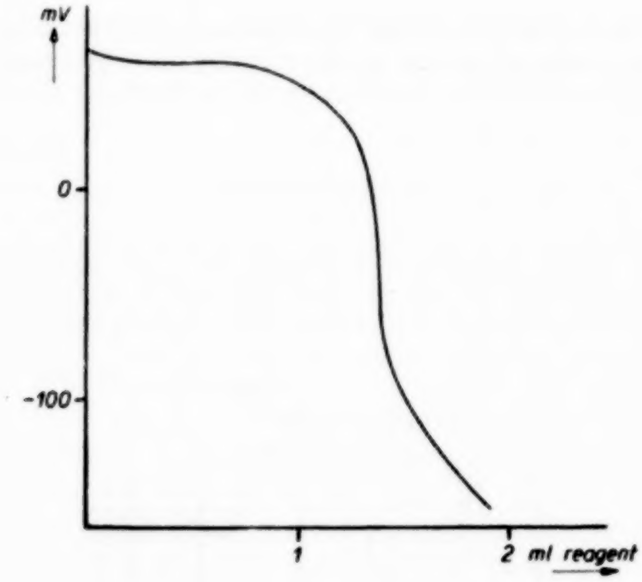

Fig. 1

CONCLUSIONS

From the results the following conclusions may be drawn:

1. The satisfactory agreement between the calculated values and the values found proves that the reaction between CS_2 and ethanolic KOH to form potassium ethyl xanthate is rapid and quantitative.
2. The reaction between potassium ethyl xanthate and Cu^{+2} is so rapid as to ensure a quick establishment of the E.M.F.
3. Potassium ethyl xanthate decomposes at a pH under 5.8.

4. There is no reason to assume that the carbon disulphide used in the preparation of the standard solution contains less than 100% CS_2.
5. In view of foregoing conclusions it may be said that CS_2 can be determined with good precision (standard deviation = 0.039 mg of CS_2).

ACKNOWLEDGEMENT

The author wishes to thank Prof. Dr. E. VAN DALEN, Free University, Amsterdam, for his helpful interest and encouragement during this investigation and the management of the N.V. Onderzoekingsinstituut "Research" for permission to publish this paper.

SUMMARY

A potentiometric determination of potassium ethyl xanthate with Cu(II)-acetate is described. From the results it follows that CS_2 reacts quantitatively with ethanolic KOH to give potassium ethyl xanthate. The method may therefore be used for the determination of CS_2.

RÉSUMÉ

Une méthode potentiométrique est décrite pour le dosage de l'éthylxanthogénate de potassium au moyen de l'acétate de cuivre. Les résultats prouvent que la formation de l'éthylxanthogénate de potassium, à partir du sulfure de carbone et de l'hydroxyde de potassium, en solution alcoolique est quantitative. La méthode proposée peut donc être utilisée pour le dosage du sulfure de carbone.

ZUSAMMENFASSUNG

Es wird die potentiometrische Bestimmung von Kalium-äthylxanthogenat mit Kupfer(II)acetat beschrieben. Die Resultate zeigen, dass CS_2 quantitativ mit äthanolischer Kalilauge reagiert, um Kaliumäthylxanthogenat zu bilden. Folglich kann die Methode für die Bestimmung von CS_2 verwendet werden.

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IODIMETRIC ESTIMATION OF ASCORBIC ACID WITH THE PLATINUM-TUNGSTEN BIMETALLIC ELECTRODE SYSTEM

by

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INTRODUCTION

Although a platinum electrode immersed in an oxidation-reduction solution indicates the reversible potential of the system, a tungsten electrode does not do so[1-4]. At equivalence therefore, whereas the potential of the Pt electrode varies suddenly, that of the W electrode remains unchanged. The Pt-W bimetallic electrode system, successful in inorganic oxidation-reduction electroanalysis, has recently been extended[5] in this laboratory to the estimation, by the bromination method, of readily and quantitatively brominated organic compounds, *e.g.* aromatic amines, phenols, *etc.* It appeared of interest therefore, to investigate the applicability of the system to the iodimetric estimation of ascorbic acid as recommended in the B.P.[6].

EXPERIMENTAL

The experimental arrangement and the electrical circuit are shown in Fig. 1. A Pyrex cell C fitted with Pt and W electrodes, a source of constant e.m.f. (1.5 volts) E, a variable resistance R (1.5 kΩ) and a sensitive galvanometer G were connected in series. The resistance R was adjusted initially, with C excluded, for full scale deflexion of the galvanometer. AnalaR grade ascorbic acid was further purified by repeated crystallization. A weighed amount (0.05-0.15 g) of the pure substance dissolved in water and acidified with sulphuric acid to a $2N$ solution was taken in C. Galvanometer deflexions were noted after successive additions, from a burette, of small amounts of a standard iodine solution and thorough mixing. Observations were continued, in each case, beyond the point of equivalence. Volumetric glass-ware used were of NPL class A standard. The temperature of the cell, the solutions and the measuring vessels was maintained at 25.0 ± 0.2° C in an air thermostat. A representative set of results is shown graphically in Fig. 2.

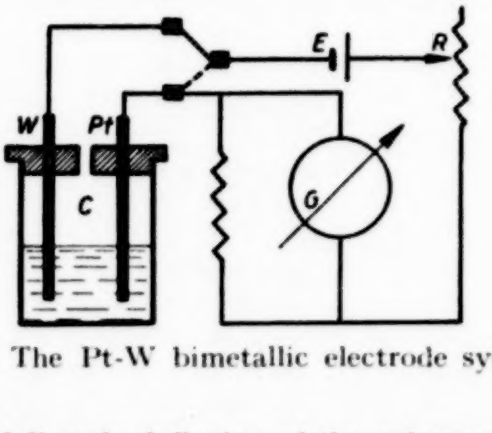

Fig. 1. The Pt-W bimetallic electrode system.

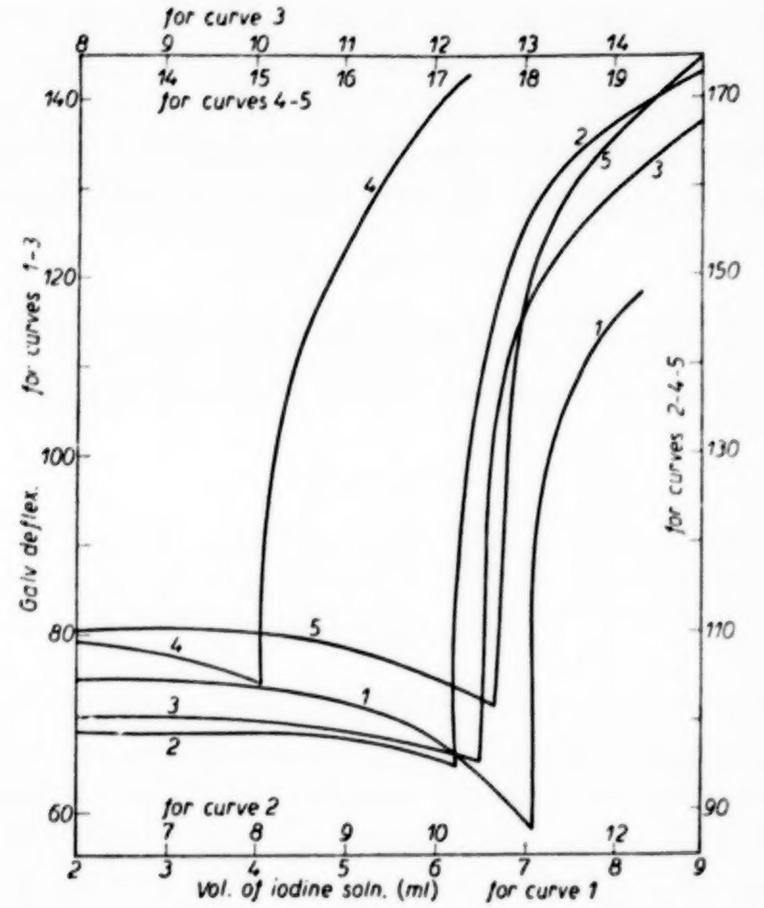

Fig. 2. Estimation of ascorbic acid with the Pt-W bimetallic system (curve 1, 0.0574 g; 2, 0.0828 g; 3, 0.1020 g; 4, 0.1218 g; 5, 0.1430 g).

DISCUSSION OF THE RESULTS

Each curve in Fig. 2 is characterized by a markedly defined break, the position of which corresponds quantitatively to the amount of iodine required by the reaction

$$C_6H_8O_6 + I_2 = C_6H_6O_6 + 2\ HI.$$

The weights of ascorbic acid taken and those calculated are contained in Table I.

TABLE I

Wt. of ascorbic acid (g) Taken	Found	Error
0.0574	0.05718	−0.00022
0.0828	0.08271	−0.00009
0.1020	0.1013	−0.0007
0.1218	0.1219	+0.0001
0.1430	0.1431	+0.0001

An examination of data in Table I shows that the error is generally far less than that usually met with in ordinary volumetric estimations; this is indicative of the fact that the Pt-W bimetallic electrode system is applicable to the quantitative determination of ascorbic acid by the iodimetric method.

References p. 589

ACKNOWLEDGEMENT

Grateful thanks of the authors are due to Prof. S. S. JOSHI for his kind interest in the work.

SUMMARY

The Pt-W bimetallic electrode system is applicable to the quantitative iodimetric estimation of ascorbic acid. Errors are far less than those usually met with in ordinary volumetric analysis.

RÉSUMÉ

L'électrode bimétallique platine-tungstène peut être utilisée pour le dosage iodométrique de l'acide ascorbique. Les erreurs faites sont beaucoup plus faibles que celles observées lors des analyses volumétriques ordinaires.

ZUSAMMENFASSUNG

Die bimetallische Platin-Wolfram-Elektrode kann für die jodometrische Bestimmung der Ascorbinsäure verwendet werden. Die Fehler sind viel kleiner, als diejenigen der gewöhnlichen volumetrischen Analysen.

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BOOK REVIEWS

Analyse Qualitative Minérale by **Paul-E. Wenger, Denys Monnier and Yvonne Rusconi**, Georg et Cie S.A., Genève, 1955, xviii + 315 pp. Fr.s. 25.—

Although it is not actually stated, this work may be considered to be a revision and amplification of *Traité de Chimie Analytique Qualitative Minérale* by Wenger, Duckert and Rusconi (1946).

It is based on the classical method of group separations but has many novel features: full use is made of microchemical reactions and organic reagents. Since Prof. **Wenger** has long been a member of the I.U.P.A.C. New Analytical Reagents Commission it goes without saying that only the best and well authenticated reactions are recommended.

The first part of the book (59 pages) deals with fundamental principles of importance to analysis, such as electrolytic dissociation, modern theories of acids and bases, oxidation-reduction, solubility product, induced and masked reactions. There follow the principal reactions of the cations (arranged in the order of conventional group analysis) and of the anions (190 pages). In the final practical part (55 pages) very valuable and detailed instructions are given for the treatment of unknown substances submitted for analysis. It is usually this part which gives so much trouble to the student, particularly when dealing with insoluble and intractable substances. He will find here very real practical guidance, obviously based on the authors' wide experience.

There are, in addition, tables giving dissociation constants, solubilities of salts, redox potentials, etc. The book is well produced, with stiff cloth-covered boards.

The reviewer would conclude by echoing the words of Prof. G. **Charlot** in the Preface: "C'est donc en toute confiance que l'on peut souhaiter la bienvenue à cette nouvelle édition".

N. Strafford (Manchester)

Introduction to paper electrophoresis and related methods, by **Michael Lederer**, Elsevier Publishing Company, Amsterdam, Houston London, New York, 1955 xii + 206 pp., 70 illus., 37s, 6d.

Paper electrophoresis was first employed as a method for the separation of proteins. It has later been shown that the technique can be successfully applied to widely different classes of substances. Dr. **Lederer** emphasizes this fact and omits a comprehensive review of the literature in favour of clarity.

After a short historical part, some electrochemical laws necessary for an understanding of the principles, and an outline of the theory of apparatus and the general aspects of the techniques are described. In this connection continuous electrophoresis and electrophoresis combined with chromatography are also dealt with. The applications of paper electrophoresis are treated in eleven chapters. Some of these review a few publications only, and it can be questioned if they merit a whole chapter. One chapter deals with physicochemical measurements, *i.e.* mobility and isoelectric point determinations. In the last part of the book some related methods are described. First, an account is given of zone electrophoresis in columns and throughs using supports such as glass beads, starch and cellulose powder. Zone electrophoresis inside gels is described in detail in the following chapter. The two final chapters deal with measurement of diffusion rates inside porous media and electrokinetic ultrafiltration, respectively.

The development of electrophoresis in stabilizing media into a routine method in numerous laboratories and the rapid increase in the number of publications has made a systematic treatise like Dr. **Lederer**'s very welcome. A somewhat more critical treatment of the material would have been valuable, but the reviewer is aware of the fact that the meagre information often available from the publications makes such a treatment difficult.

The book is well written and the contents well organized, and it can be recommended as an introduction to the field of zone electrophoresis and as a reference book for the research worker interested in separation methods.

Per Flodin (Uppsala)

Mises au point de chimie analytique pure et appliquée et d'analyse bromatologique, publiées sous la direction de J. A. GAUTIER, Troisième série, Masson et Cie., Paris 1955. Un volume broché de 192 pages avec 48 figures. Prix: Fr. 1900.—.

Il s'agit d'une collection de conférences intéressantes faites à la Faculté de Pharmacie de Paris pendant l'année 1954-1955. Elle débute par une étude de DIDIER BERTRAND sur les oligo-éléments des denrées alimentaires et leur rôle nutritionnel. Ensuite, HENRI GUÉRIN donne une sélection d'analyses et de micro-analyses des gaz en insistant sur les méthodes récentes: films de savon, conduction thermique, magnétisme, infrarouge, spectrographie de masses. La plupart des données et schémas sont extraits de l'excellent traité du même auteur (Masson et Cie., Editeurs). On passe alors à une intéressante mise au point d'EDGAR LEDERER sur les acquisitions récentes en chromatographie (125 références des deux dernières années) en portant l'attention sur les séparations de produits biologiques. Une conférence de FERNAND PELLERIN nous rappelle les grands principes des dosages acidimétriques dans les solvants non aqueux tandis que JEAN PIEN passe en revue les méthodes connues pour le dosage de la matière grasse du lait.

Cependant, l'originalité et l'utilité de cette brochure portent sur l'article final dû à RENÉ POTTIER, relatif à la *documentation en chimie analytique*. Je l'ai déjà consulté plusieurs fois y trouvant toujours le renseignement cherché. Il ne s'agit pas là d'une sèche énumération de livres relatifs à la chimie analytique mais de leur présentation raisonnée, travail considérable qui porte peut-être sur une vingtaine ou une trentaine d'années. L'utilité de cet article est incontestable et il faut remercier l'auteur d'avoir bien voulu le laisser extirper de ses fichiers. Je lui ferai un tout petit reproche, celui de n'avoir pas mis l'accent suffisant sur le travail considérable que des savants consciencieux comme WENGER, GILLIS et VAN NIEUWENBURG ont effectué pour réaliser le 2ème Rapport des réactifs nouveaux.

CLÉMENT DUVAL (Paris)

Spektrochemische Betriebsanalyse. Mit praktischen Ratschlägen für die Ausführung spektrochemischer Analysen im Betriebslaboratorium von DR. HEINRICH MORITZ. Ferdinand Enke Verlag, Stuttgart, 1956. Zweite verbesserte Auflage, XV und 240 Seiten mit 65 Abbildungen und 19 Zahlentafeln. Geheftet DM 52.—, Ganzleinen DM 55.—.

L'auteur nous présente un manuel pratique et fidèle d'analyse spectrale, particulièrement intéressant pour les débutants dans les laboratoires industriels.

Dans la première partie de ce traité bien conçu et remarquablement simple et clair, nous trouvons les chapitres classiques traitant des principes fondamentaux, des différentes sources d'émission, des spectrographes, des appareils pour le dépouillement des spectres, de l'émulsion photographique et des principes de la spectrométrie. Dans la seconde édition, qui vient de paraître, l'auteur a fait mention des progrès récents de la technique spectrochimique, mais un espace trop limité leur a été réservé. On regrette qu'à côté d'une description détaillée des sources classiques beaucoup utilisées en Allemagne il ne traite d'avantage les sources nouvelles et très importantes des A.R.L., de Hilger, d'Optica, etc. Les méthodes d'analyse directe, particulièrement intéressantes et supplantant peu à peu les méthodes photographiques dans toutes les industries importantes auraient mérité plus d'attention, et il nous semble qu'il existe d'autres appareils à lecture directe que ceux des Etats-Unis et de l'Italie.

Dans la deuxième partie — la plus importante — l'auteur traite successivement l'analyse qualitative, l'analyse générale et l'analyse quantitative, s'intéressant surtout aux méthodes applicables dans l'industrie. Le chapitre traitant l'analyse générale est nouveau et intéressant. Chaque chapitre traite séparément l'analyse des solutions et l'analyse des matières solides, distinguant entre métaux et alliages d'une part et matières minérales d'autre part. Toutes les manipulations sont décrites de façon claire et complète, avec plusieurs détails pratiques de grande importance, basés sur une expérience personelle de plusieurs années.

Dans la troisième partie l'auteur fait la comparaison entre l'analyse chimique et spectrochimique au point de vue durée de l'analyse et matière consommée, tandis que dans la quatrième partie il nous présente — à titre d'exemple — des conditions opératoires, essayées et appliquées avec succès à l'analyse de l'aluminium et de l'acier.

Malgré l'objection faite, le manuel peut être recommandé au spectrochimiste de tout laboratoire industriel qui y trouvera pour chaque cas particulier des renseignements utiles et très importants.

J. EEKHOUT (Gand)

Qualitative Schnellanalyse nach Charlot, von A. SCHLEICHER, 2. Auflage, Walter de Gruyter u. Co., Berlin, 1956, 90 Seiten. Geh.: DM. 7.80.

Das Buch enthält in der Hauptsache die Beschreibungen von Nachweisreaktionen für die häufigeren Kat- und Anionen. Der erste Teil ist eine Übersetzung des Buches *Analyse qualitative rapide des cations* von CHARLOT, BÉZIER u. GAUGUIN, der zweite gibt den Inhalt einer Arbeit von ODEKERKEN [*Z. anal. Chem.* 131 (1950) 165] über Nachweis von Anionen wieder. Nach den gegebenen Arbeitsvorschriften soll jedes der besprochenen Ionen neben größeren Mengen irgendeines anderen oder der Gesamtheit der anderen Ionen nachzuweisen sein. Trennungen werden nach Möglichkeit vermieden. Bei den meisten Einzelreaktionen wird auf einige Störungsmöglichkeiten hingewiesen, doch können diese, dem Umfang des Bändchens entsprechend, nicht vollständig erfaßt sein. Falls sich der Benutzer dieser Tatsache bewußt ist und ihn die Erkennung kleiner Gehalte nicht interessiert, mag der Inhalt des Buches hier und da nützlich sein.

Der analytisch arbeitende Chemiker hat schon lange, wenn nur der Nachweis einzelner Bestandteile einer Probe zur Rede stand, Trennungen und Nachweisreaktionen, die für den speziellen Fall besonders geeignet erschienen, angewandt und nicht irgendeinen Trennungsgang durchgearbeitet. Insofern kann man hier wohl kaum von einem neuen Wege sprechen, wie das der Herausgeber tut. Faßt man allerdings diesen „neuen Weg" so auf, daß man eine qualitative Analyse nun nur noch auf dem Wege einer Aneinanderreihung derartiger Einzelnachweise durchzuführen gedenkt, so ist das eine nicht zu vertretende Simplifizierung der beim praktischen analytischen Arbeiten vorliegenden Verhältnisse, die entweder auf Kosten der Nachweisempfindlichkeit oder der Eindeutigkeit des Nachweises gehen muß.

Gegenüber den grundsätzlichen Bedenken gegen die in dem Buche vertretene Tendenz sind alle nnderen Bemerkungen, die zu machen wären, von zweitrangiger Bedeutung. Die mit einer gewissen Einseitigkeit ausgewählten Nachweisreaktionen sind von unterschiedlicher Empfindlichkeit und Leistungsfähigkeit. Kleinere Unkorrektheiten finden sich an mehreren Stellen.

H. BODE (Hannover)

Technisch — chemische Analyse, von L. MEDICUS UND H. REUTHER, 6. Auflage, Theodor Steinkopff, Dresden und Leipzig, 1955, 231 Seiten, 57 Abb. DM. 9.—.

In dem vorliegenden Buche werden in kurzer, übersichtlicher Weise die wesentlichen Verfahren der technisch-chemischen Analyse besprochen. Im I. Teil werden zunächst die bei der Probenahme zu beachtenden allgemeinen Gesichtspunkte dargestellt und dann die wichtigsten technisch verwendeten Methoden der Untersuchung des Wassers, fester und flüssiger Brennstoffe, der Schmiermittel sowie die technische Gasanalyse in den Grundzügen beschrieben. Der II. Teil bringt eine Beschreibung kolorimetrischer und photometrischer Methoden, gewichtsanalytischer Schnellverfahren und gasvolumetrischer Methoden. Nach kurzer Besprechnung der Begriffe und einfacher Apparaturen werden Beispiele für die Anwendung dieser Verfahren gegeben, die so ausgewählt sind, daß sie besonderes technisches Interesse besitzen. Der III. Teil behandelt die Untersuchung der Erze (Hüttenprodukte) und Metalle sowie der Düngemittel an einigen ausgewählten Beispielen. Im Anhang sind Angaben über technische Temperaturmessungen und Messungen des pH-Wertes gemacht.

Entsprechend der Aufgabe, die sich der Bearbeiter gestellt hat, liegt das Hauptgewicht bei der Beschreibung solcher Verfahren, die mit verhältnismäßig geringen Mitteln als Routinebestimmungen im Betriebslaboratorium durchgeführt werden können, theoretische Betrachtungen sind demgemäß auf das Mindestmaß beschränkt, das zu einem anschaulichen Verständnis der Dinge ausreicht. Eine größere Anzahl von Literaturhinweisen, die sich allerdings überwiegend auf ältere Arbeiten beziehen, wird von manchem Benutzer als nützlich empfunden werden. Bei der Auswahl der einzelnen Arbeitsverfahren wurden weitgehend DIN-Vorschriften berücksichtigt.

Das Buch kann als eine für manches kleinere Betriebslaboratorium geeignete und ausreichende Sammlung von Arbeitsvorschriften empfohlen werden, daneben ist es sicherlich auch als Hilfsbuch bei der Ausbildung von Chemielaboranten und Chemotechnikern gut geeignet.

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